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H E A T

HEAT

BY

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AUTHOR OF

"SOUND, LIGHT, AND HEAT," AND "ELEMENTARY PHYSICS"



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P R E F A C E

THE present work is intended for those who have read the elementary parts of the subject, as treated in "Sound, Light, and Heat," or who are able at once to attack a more advanced work. It is an attempt to place the leading facts and principles of the subject before the student. The point of view of the writer is that of a teacher, and this will explain why certain parts are treated more elaborately than others, and why worked numerical examples occur so frequently in the text and at the end of each chapter. Such examples should not be merely copied; they are inserted because it is found that a carefully worked example proves of great use to the student, who naturally finds a difficulty in understanding the generalizations of a science.

A fair selection of the experiments described should be performed by the student. The experiments selected will depend upon the apparatus available and the time at his disposal; they should be typical. A high form of accuracy is not required at this stage; it will be sufficient if he can clearly indicate the minor corrections that have been omitted, and how such corrections would affect the results. It is believed that the description of the experiments will enable any one to repeat them; to have gone into further details would have made the work too bulky, and many details can only be mastered either by instruction in the laboratory or by the slow yet efficient method of trial and failure. Fortunately, the once prevalent method of studying a science

from a text-book alone is rapidly disappearing. It is necessary, however, to point out that too much, as well as too little, time may be spent over experimental science ; mental inertia is as possible in the laboratory as in the lecture-room.

Lack of apparatus and skill in manipulation will prevent the verification of some experiments ; for example, Regnault's experiments on the absolute expansion of mercury in § 32 ; but there is no reason why the method should not be thoroughly understood after the simple experiments illustrated in Figs. 26 and 27 have been made. There may appear, at first sight, no reason for inserting in a book like this formulæ similar to those given on p. 43, or for refinements such as true coefficient of expansion at t° . The student will, however, meet with these in his reading, especially if he refers, as it is trusted he will do, to more elaborate treatises and to original memoirs ; this is dealt with on the first part of p. 46, and in other parts of the work.

Reference has been made to the work of recent experimenters where the results could be incorporated in a book of this design. Other examples of recent research have been omitted, as unsuitable in their present stage of development.

The permission of the publishers to use any of their blocks has made the task of illustrating the book much easier than it otherwise would have been. Some cuts have been utilized from "Sound, Light, and Heat," and thirty-five have been engraved specially.

For figures and tables, reference has generally been made to Everett's "Physical Constants ;" and to Jamin's "Cours de Physique."

§ 74 is inserted so that the student may revise his knowledge of dynamics, and to lead up to § 75, which was written to enable the reader to deal readily with results given by different experimenters in varying units. This is especially applicable to results in conductivity (§ 146).

There has been no attempt to restrict the examples or explanations to the C.G.S. units. Such a restriction may prove useful when the units are universally adopted, but at present it is necessary that other units in common use

should be understood, and the change from one set to another is a matter of easy arithmetic.

The chapter on Thermo-Dynamics is of an elementary kind, and is taken up with an attempt to explain and illustrate by examples the first two laws and the meaning of Joule's and Thomson's experiments. The published papers¹ of both should be consulted for further details; these papers will be available for many students.

The last chapter illustrates many portions of the subject of heat. Professor James Thomson's theory of atmospheric circulation has been followed, as being the most consistent of the theories on this subject.

M. R. W.

NEWCASTLE-UPON-TYNE,
May, 1893.

¹ "Mathematical and Physical Papers," by Sir Wm. Thomson.

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HEAT.

CHAPTER I.

HEAT—TEMPERATURE—THERMOMETERS.

1. Temperature.—Terms connected with the subject of heat are numerous in our ordinary language: “hot,” “cold,” “warm,” and others suggest themselves. The words are used to describe certain sensations; the agent which produces the sensations is called Heat. The word we use to describe a particular sensation depends upon the state of our body and upon our previous experience. In winter we describe a day as warm, while in summer we should describe a similar day as being cold. The water from the tap, as it runs over our hand, is said ordinarily to be cold; if the hand has previously been used to mix ice or ice and salt, the water feels agreeably warm. Not only does our opinion vary from time to time, but each hand may lead to a different decision; for example, if the right hand be plunged into water as hot as we can bear it, and the left hand be plunged into melting ice, and then both be placed in water just taken from the tap, the right hand feels cold and the left hand warm.

The state a body is in with respect to the heat that affects the senses is called in ordinary language its Temperature.

For the above reasons the hands cannot be used for the purpose of comparing temperatures. When we touch an object, the opinion we come to with respect to the temperature not only depends upon the temperature of the object, but also upon the rate at which heat is transferred from the object to the hand, or from our hand to the object. The transference of heat by conduction is readily illustrated by placing

the poker in the fire. The heat of the fire travels along the poker from the end in the fire, from particle to particle, until the temperature of the other end rises. This method of transference of heat is called Conduction.

If a short poker and a piece of wood of equal lengths be placed in the fire, the end of the poker out of the fire soon becomes so hot that we dare not touch it; the end of the piece of wood, on the contrary, can easily be retained in the hand; and we conclude that iron is a good conductor of heat, and wood a poor conductor; wool, felt, etc., are worse conductors of heat than wood.

If we touch pieces of wool (the carpet) and pieces of metal (fender, etc.) in a room without a fire and shaded from the sun, the iron feels cold and the wool warm; it will be shown later that both are at the same temperature. The reason for the different effects is that both are below the temperature of the hand. Heat flows from the hand to the metal, and is readily conducted to other parts; more heat leaves the hand, and the sensation of cold is the result. In the case of the wool, the heat flows from the hand to the carpet, but is not readily conducted to other parts of the carpet, so that the portion touched by the hand soon begins to feel warm. If the metal and wool were above the temperature of the hand, heat would flow from the part of the metal touched to the hand, and from other parts of the metal to the part touched, thence to the hand, and the metal would feel warm. In the case of the flannel this would not be so apparent; heat would simply be transferred from the part touched to the hand, but it would flow very slowly from the other parts of the flannel to the particular part touched, and thus the flannel would not feel as hot as the metal.

The difficulty of comparing temperatures is not so great when we deal with objects all made of the same substance. Bath attendants can determine with great accuracy the suitable temperature for a bath, and we can readily arrange pieces of silver or pieces of copper according to their temperature.

The temperature does not depend upon the amount of heat. If we take a pint of water from a cistern of water, both are at

the same temperature, and yet the pint contains less heat than that left in the cistern. An analogous state of things exists in the terms “level” and “quantity” of water.

If two vessels, A and B (Fig. 1), containing any liquid, be connected by a tube, the flow is determined, not by the amount of water in A and B, but by the respective levels; if the level of the water in A be higher than that in B, water flows from A to B; if the level in B be higher than in A, the flow is from B to A. If we attend only to the direction of the flow, and the two vessels be hidden from our view, then obviously we can come to no conclusion as to the quantities of water in the two vessels, but can only determine in which the level is higher. So with two substances placed in contact: if heat flows from A to B, we know that the temperature of A is higher than B; the flow of heat gives no information as to the respective quantities of heat in A and B. The flow of heat leads to a more accurate definition of temperature.

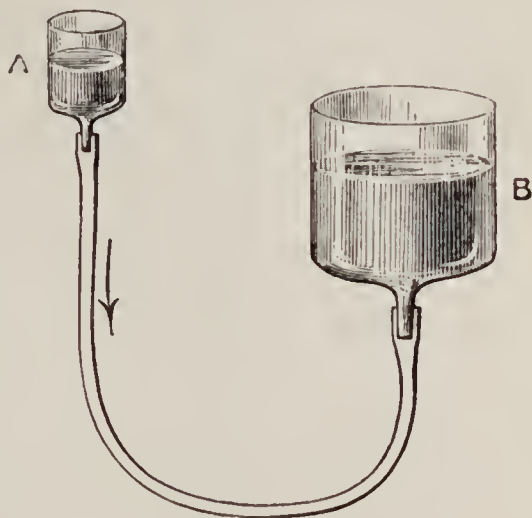


FIG. 1.

The temperature of a body is its thermal state with reference to its power of communicating heat to other bodies.

2. Expansion.—In constructing ordinary thermometers, or measurers of temperature, advantage is taken of the fact that one effect of heat upon substances is to change their volume.

Solids.—Change in length is allowed for in bridges: one end at least is not fixed, but is placed upon rollers to allow for increase in length as the temperature rises. For a similar reason space is left between the ends of rails on the railway; fire-bars are fixed loosely in fire-grates; and we note also that telegraph wires “sag” more in summer than in winter.

The following experiment illustrates linear expansion.

An iron rod about 18 inches long rests upon two blocks of

wood (Fig. 2). One end is fixed by a heavy weight, the other rests upon a fine needle. A straw is fixed at right angles to the needle with sealing-wax, and behind the index there is

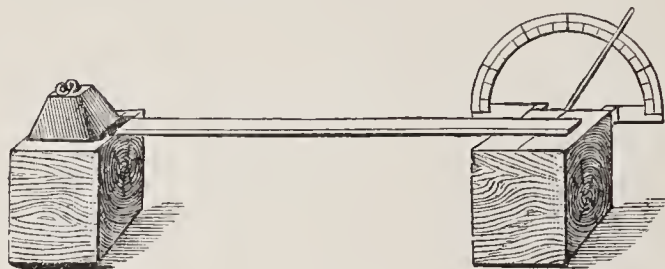


FIG. 2.

a divided cardboard scale. At the beginning of the experiment arrange so that the straw is vertical, and heat the bar with a spirit-lamp; the index moves to the right, proving that the bar is expanding, and is rolling on the needle. The iron bar can be replaced by bars of brass, copper, glass, etc.

The historical experiment of Gravesande conveniently demonstrates the cubical expansion of solids.

A brass ball, *a* (Fig. 3), when cold, is able to pass through the ring *m*; after heating, it is unable in any position to pass through.

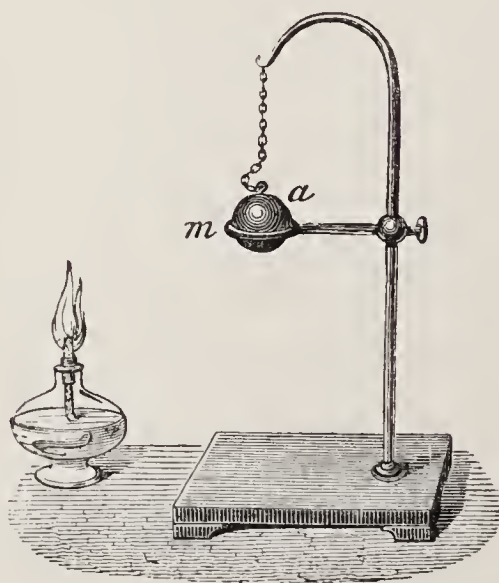


FIG. 3.



FIG. 4.

Liquids.—The expansion of liquids can be observed by enclosing them in glass vessels. A 2-oz. flask is filled with water coloured with red ink or other colouring matter (Fig. 4).

The flask is closed with a cork, through which passes a fine tube about 12 inches long: on inserting the cork, the water rises slightly up the tube. A strip of paper ruled with lines at equal distances, placed behind the tube, serves for a scale.

On placing the flask in a dish of warm water, you can observe (*a*) a slight descent of the liquid, followed by (*b*) a gradual ascent.

The descent is due to the fact already ascertained, that solids expand on being heated. The heat first affects the flask, increases its volume, and there is consequently a descent of the liquid. As soon as the heat reaches the water, it expands, and at a greater rate than the glass does, and therefore the liquid rises up the tube. Liquids, we conclude, expand more than solids.

By fitting up two similar pieces of apparatus, using alcohol and mercury as the liquids, we can roughly compare the expansion of water, alcohol, and mercury. Slightly adjusting the corks, we can arrange so that at the ordinary temperature the liquids stand at the same height in each tube. Place all three in a basin of lukewarm water. The alcohol rises higher than the water, and the water than the mercury; observe, however, that the mercury begins to rise, and reaches to its highest point first.

In dealing with solids, high temperatures (that from flame) and means of multiplying effects were necessary to demonstrate expansion; in liquids the effect is at once observable, even when the difference of temperature is not great. By selecting a tube whose diameter is small compared with that of the flask, we can the more readily observe the effects. Liquids enclosed in glass vessels provided with fine tubes are therefore used in the construction of thermometers.

3. Thermometers.—*The Mercurial Thermometer.*—A clean tube (whose bore we shall assume is a perfect cylinder) is closed at one end, and a small bulb, generally of cylindrical form, is blown. The bulb is gently heated, and part of the air is expelled; the open end is then dipped into mercury; as the air in the tube cools, a small amount of mercury is forced into the bulb. The operation is repeated until sufficient mercury

is observed in the bulb. The bulb is then heated until the mercury boils; the mercury vapour drives out all the air and moisture. The end is again dipped into mercury while heat is being applied, and the tube fixed until it cools. The pressure of the atmosphere forces the mercury into the tube, and it is found that the bulb and tube are filled with mercury, and mercury only. If any air be present, the operation is repeated until the bulb and tube are completely filled. The glass is carefully softened and drawn out where it is intended to close the tube; when cold the tube is cut off, leaving a very fine aperture.

We must now determine the highest temperature the particular thermometer is required to measure. For example, if the instrument will never be used for any temperature above boiling water, it may be placed in a bath of strong brine or of acetic acid; if intended to indicate higher temperatures, a bath of aniline may be used; for yet higher temperatures, strong sulphuric acid. The bath is heated to boiling point, the mercury expands, and part escapes; when the bath boils steadily no more mercury will be expelled. The fine end is softened and closed with a small blow-pipe flame, the lamp is removed from the bath, and all is allowed to cool. The instrument now contains mercury and mercury vapour (Fig. 5). In the best thermometers the bulb is cylindrical.



FIG. 5.

4. The Fixed Points.—It is found that the temperature of melting ice is the same whenever and wherever the experiment is tried (it is affected by changes of pressure (see § 91), but so slightly that the change can be neglected in constructing thermometers), and that the temperature of steam is always constant if the pressure be constant. These two temperatures determine the two fixed points of the thermometer—(a) the freezing point and (b) the boiling point of water.

(a) *The Freezing Point.*—Clean ice is placed in a vessel (preferably made of a substance that is a poor conductor of heat; for example, of wood encased in felt) (Fig. 6). The experiment must be conducted in a room whose temperature

is above that of melting ice ; the water formed escapes freely at the bottom of the vessel. The closed thermometer is inserted so that the bulb and nearly the whole of the stem is surrounded with ice, and the whole is left for about a quarter of an hour. The tube is then moved so that the mercury is just visible above the ice. When its position remains steady, a scratch is made on the glass, and the point marked is called the freezing point.

(b) *The Boiling Point.*—The bulb is placed in a metallic vessel, M, with a narrow upper part, A. This narrower portion is surrounded by another vessel, B (Figs. 7 and 8). The thermometer t is passed through the cork a . By following the course of the arrows in the section, it is seen that steam



FIG. 6.

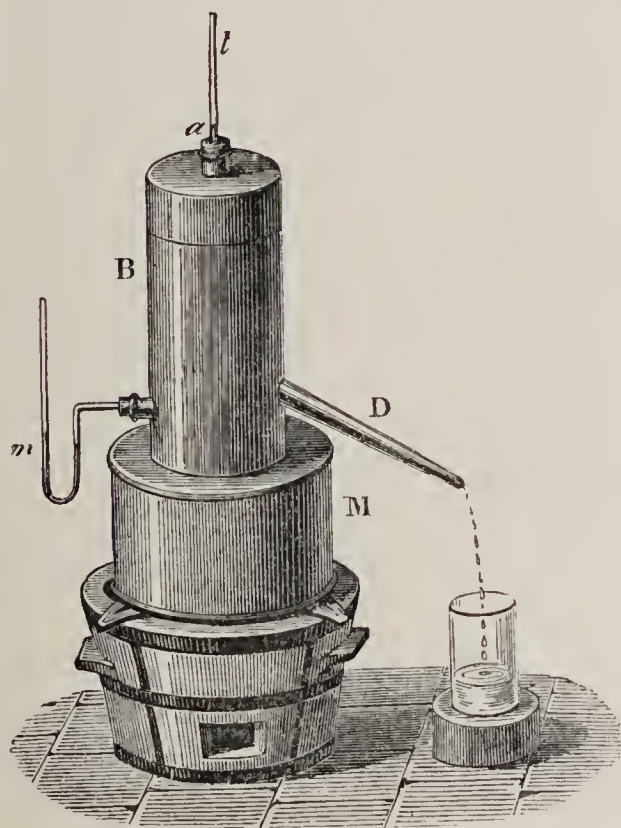


FIG. 7.

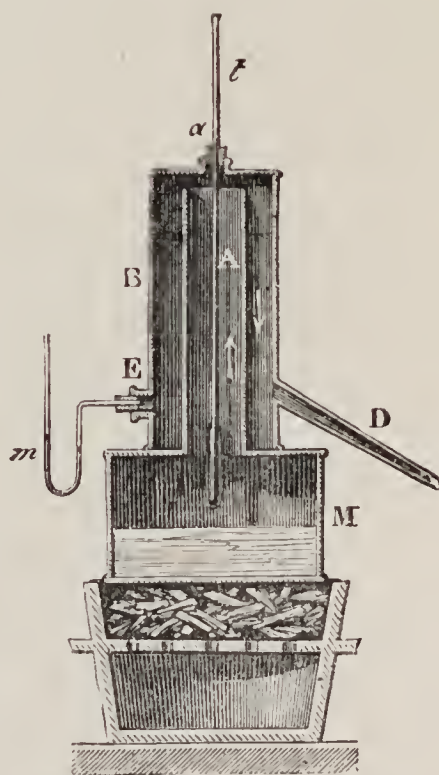


FIG. 8.

from the boiling water in M surrounds the inner tube and prevents it cooling; the steam escapes by the tube D, the orifice of which should be large enough to prevent any increase of pressure inside the vessel. The small tube *m*, inserted in B by the cork E, contains mercury, and serves as a pressure gauge: the mercury in both limbs should be level throughout the experiment. The temperature of boiling water depends upon the substance of which the vessel is made, and also depends upon any impurities in the water, but the temperature of steam depends only upon the pressure; the bulb should therefore not dip into the water, but should be slightly above it. The pressure is measured by the barometer. After the pure water has boiled some time, the tube is moved so that the top of the column of mercury can just be seen; when its position remains steady, a mark is made upon the glass, and the barometer is read (the mercury in the tube *m* should be at the same in each branch).

In England the *boiling point is the temperature of steam at the pressure of 29.905 inches of mercury at freezing point at the sea-level in the latitude of London.*

These conditions cannot ordinarily be fulfilled in practice, and corrections must be made (see Table, § 99). The points involved in this definition of boiling point will be discussed later; at present we can assume that the boiling point as obtained in the experiment satisfies the conditions.

5. The Scales.—At the temperature of freezing point the mercury fills the bulb and the stem up to freezing point; at the temperature of the boiling point the volume of mercury enclosed in glass expands, the increase in volume being represented by a thread of mercury extending from freezing point to boiling point.

The distance between the two fixed points is divided into equal parts, called degrees. Three methods are followed.

(1) *Fahrenheit's Scale.*—The lower point is numbered 32 (called 32 degrees, written 32°), the upper 212 (written 212°). The distance between the points is divided into 180 equal parts, and the graduation is continued above and below the points. The thirty-second division below the freezing

point is marked 0, and is called zero; below this we have minus 1 degree (written -1°), etc. It is stated that Fahrenheit took for the zero of his scale the lowest temperature he obtained by mixing ice and salt. This scale is in common use in England and America for ordinary and meteorological purposes.

(2) *Centigrade Scale*.—The boiling point is the temperature of steam at 760 millimetres of mercury pressure at 0° Centigrade at the sea-level in latitude 45° N., equivalent to the 29.905 inches of mercury reduced to freezing point at the sea-level in the latitude of London.

The freezing point is called 0° , the boiling point 100° , and the graduation is continued above and below (-10° , etc.) these points.

This scale is used generally on the continent, and in England for scientific purposes.

(3) *Reaumur's Scale*.—Freezing point is marked 0° , boiling point 80° . This scale is in use in Russia and in Germany for commercial and household purposes.

Changing the readings from one scale to another is readily done. Imagine three exactly similar thermometers graduated by the three methods, as in Fig. 9. In order to compare the readings when the mercury is at the height x , y , we have, if f , c , and r represent the number of degrees marked in each scale—

$$\frac{f-32}{180} = \frac{c}{100} = \frac{r}{80}$$

seeing that the numerator and the denominator of each fraction represent the same distance.

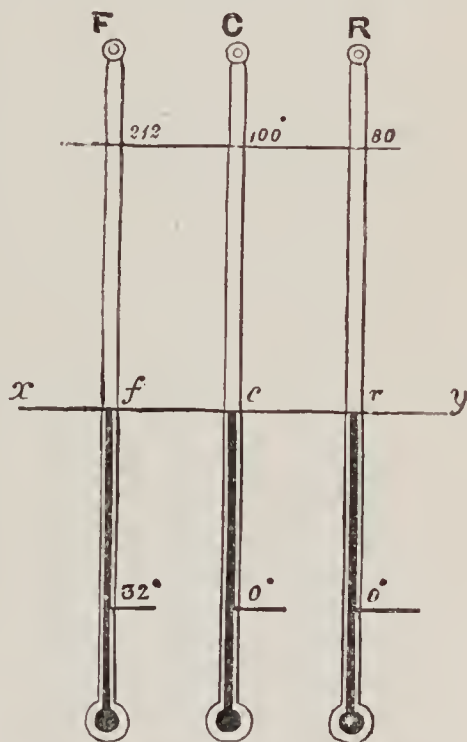


FIG. 9.

We easily deduce—

$$f = \frac{9}{5}c + 32$$

$$f = \frac{9}{4}r + 32$$

$$c = \frac{5}{9}(f - 32)$$

$$c = \frac{5}{4}r$$

$$r = \frac{4}{9}(f - 32)$$

$$r = \frac{4}{5}c$$

6. Calibration of the Tube.—In the construction of the thermometer several assumptions were made that will not prove true in practice. In instruments of precision, therefore, corrections have to be made.

The tube is not generally a perfect cylinder; in dividing the distance between the fixed points equal lengths will not necessarily represent equal volumes; to correct this error the tube is calibrated. A good tube should be selected, a preliminary trial being made as follows: A column of mercury about 2 inches long is drawn into the tube, and its length is exactly measured; the column is moved slightly, and the length is again measured; and this process is continued along the tube. The mercury fills the same volume each time, and if there be a variation in the length exceeding 0.04 inch, the tube should be rejected.

Into a good tube a column of mercury about $\frac{1}{2}$ inch long is introduced, say A C (Fig. 10), the points A, C are carefully

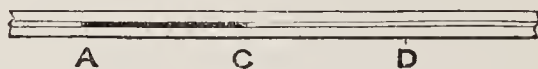


FIG. 10.

marked. The column is now moved until the end that was at A comes to C, the other end being at D. Evidently the volume A C equals the volume C D. The end is then moved to D, and so on, until the tube is divided into parts of equal capacity. Each of these parts is divided into a convenient number of equal parts, it being assumed that the diameter of the tube remains uniform for any one of the distances. Suppose such a tube be made into a thermometer, and that when the two fixed points are determined, it is found that they include between them 214.5 of the tube-divisions, then each

division Centigrade is equal to 2.145 of the tube-divisions. Thus 50°C. will be 107.25 from the freezing point, etc.

The following method may be used after the thermometer is made, and is sufficiently accurate for most purposes.

Suppose 0° and 100° Centigrade have been determined in the usual way. The thermometer is placed in a temperature nearly 50°C. , and the thread rises to about C (Fig. 11). By heating slightly at A, the thread A C can be separated from the remaining mercury in the tube. Allow all to cool. Move the thread so that the end comes to B, and note the position of the other end at C_1 ; move the thread so that one end is at 0 (A), the other being at C_2 ; bisect the distance C_1C_2 in the point C: this can be done with sufficient accuracy by the eye. Then C is the true 50° . Proceed similarly to divide the 50° , so as to find 25° and 75° , and divide each 25 into 25 equal parts.

The marks for the divisions are made as follows: The stem is covered with a thin coating of wax; the distance between any two points is divided by the dividing-machine (or simply by placing the tube along a scale); the machine removes the wax at each point. The whole is then subjected to the vapour of hydro-fluoric acid, which etches the glass where the wax has been removed.

7. Variation of the Fixed Points.—When thermometers are tested periodically, it is found that the zero changes—its position rises in the stem. The reason is that glass, after being heated, does not readily return to its original molecular condition; the greatest part of the contraction takes place as the glass cools, but a small amount of the contraction continues for some time, and may extend over years. A thermometer marked accurately at first, when tested after a few years may show the zero a few tenths of a degree above the original zero. If the freezing point has risen say 0.3° , then a reading of 20.6° is really 20.3° .

Again, if a thermometer be subjected to a high temperature, say the boiling point of water, and if immediately after



FIG. 11

the freezing point (or any low temperature) be determined, the glass will not have got back to its original state, and a temperature noted by this thermometer will be too low. It is on this account that the freezing point is determined first.

These errors will be diminished (1) if the glass be properly annealed; (2) if the bulbs be made some time before being filled; and (3) if the graduation is delayed some time after the filling. The freezing point should, of course, be determined before the boiling point.

The thermometer must be used in the vertical position if the fixed points have been determined while the stem was vertical. Some thermometers are used in a horizontal position (§ 11); their fixed points must be found in this position. In the vertical position the pressure of the column of mercury not only compresses the mercury, but also will enlarge the bulb, so that the reading in the horizontal position will always be higher than that in the vertical position.

8. Small Corrections.—In taking the temperature of a substance, not only the bulb, but also the stem must be exposed to the required temperature, otherwise the reading will be too low. The method of correcting this error will be taken after expansion.

A thermometer graduated at the ordinary pressure, if enclosed in a vacuum, will show a reading below the true reading, because relieving the pressure on the bulb causes the bulb to expand, and thus the mercury sinks.

In graduating the thermometer we assume that mercury in glass expands the same fraction of its volume per degree when its temperature rises from 0° to 100° C. as it does from 10° to 20° or 90° to 100° . This is very nearly the truth in the case of mercury between 0° and 100° , and slightly above and below these temperatures. In the case of water and alcohol this regularity does not occur in their expansion. For this reason a water thermometer graduated to agree with a mercury thermometer at 0° and 80° C. would not indicate 40° C. when the mercury thermometer stood at 40° . This will be the more readily understood after §§ 33 and 36.

9. Standard Thermometers.—The graduation of

thermometers is seen to be a long, tedious, and difficult process. Fortunately, all the corrections are not necessary. The work has been carefully done on certain standard thermometers kept at Kew, and any other thermometer can be compared with a standard thermometer by subjecting both to the same temperature, and marking on the ordinary thermometer the temperature indicated by the standard thermometer, just as the alcohol thermometer is compared with a mercury thermometer. This is analogous to testing ordinary weights and measures by comparing them with the standard Government weights and measures. If the thermometer be already graduated, then a table can be constructed showing how its readings differ from those of the standard thermometer.

10. Alcohol Thermometer.—Mercury freezes at about -40° C., and its rate of expansion for some degrees above this is not nearly equal to its rate of expansion from 0° to 100° . A mercury thermometer cannot, therefore, be used for low temperatures. Alcohol has not as yet been frozen; it boils at 80° C. It is, therefore, a suitable liquid for low temperatures. The method of construction is similar to that of making a mercury thermometer. The freezing point can be determined as above. The freezing point of mercury, -40° , would give another low point. It is generally graduated by comparing it with a standard mercury thermometer between 60° C. and -20° C., and continuing the divisions below -20° .

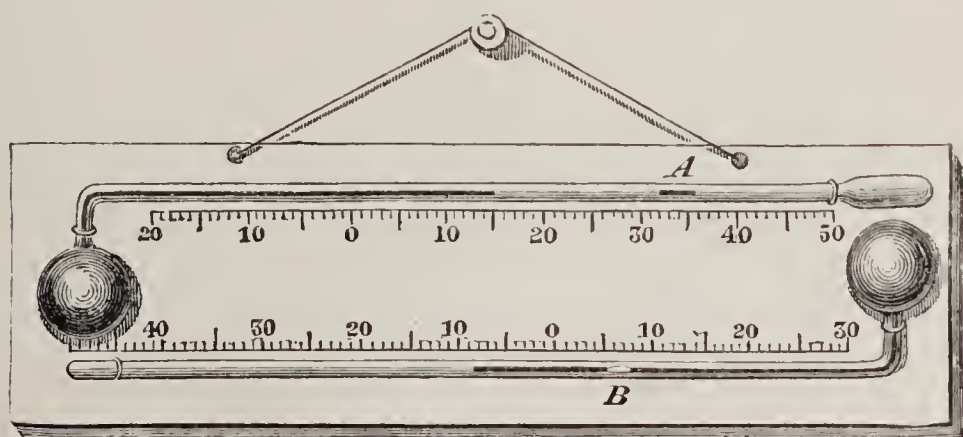


FIG. 12.

11. Maximum and Minimum Thermometers.—For many purposes (mostly meteorological) the highest and lowest

temperatures during certain periods are needed. To effect this, maximum and minimum thermometers are used.

An ordinary mercurial thermometer is graduated when in a horizontal position. It contains in the tube a small cylinder of iron (*A*, Figs. 12 and 13). When the temperature rises, the mercury pushes the iron before it; when the temperature falls, as the mercury does not wet the iron, the column retires and leaves the iron behind it. The position of the end of the iron nearest to the mercury

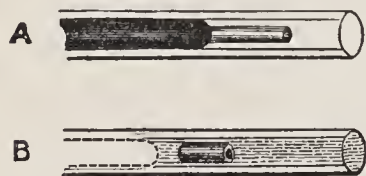


FIG. 13.

determines the maximum temperature.

In the minimum thermometer the liquid is alcohol, and the index is made of coloured glass (*B*, Figs. 12 and 13). The index is immersed in the liquid so that the concave surface of the alcohol touches one end of it. When the temperature rises, the liquid flows past the index without displacing it; when the temperature falls, the alcohol retreats, and, the concave surface not being easily broken, pushes back the index.

The above *Rutherford thermometers* are only useful when the instrument can be kept horizontal.

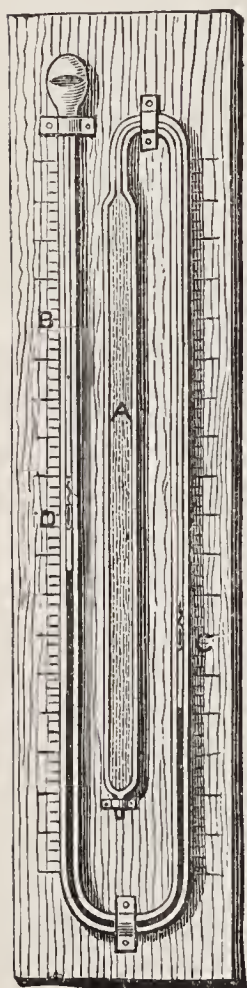


FIG. 14.



In *Six's thermometer* the tube is bent as in Fig. 14. The part *A* is filled with alcohol, and is cut off from the part *B* by a thread of mercury. *B* contains alcohol and alcohol vapour. Above the mercury in each branch of the tube is a small iron index (*C* and *D*) covered with glass. Each index slides easily in the tube, but by the aid of slight springs of glass they are kept upright, and only move when a slight pressure is exerted (*E*, Fig. 14). The

indices are brought into contact with the columns of mercury,

by the help of a small magnet. If the alcohol in A expands, the mercury in B rises and pushes forward the index. When A contracts, the mercury falls, but the springs keep the index in position, the mercury easily flowing past it. Thus the lower part of the index D indicates a maximum temperature, and it is readily seen that the position of the lower part of the index C indicates a minimum temperature.

12. Thermographs.—The above forms lack the accuracy which is obtainable by the *self-registering thermometers*. In one form an ordinary thermometer tube is placed in front of a narrow slit so that light can only pass where there is no mercury. If light from a lamp be directed upon the slit, and behind it there be placed a cylinder of sensitive paper, so arranged that the paper is unwound at a certain rate, the mechanism being regulated by clockwork, then, when the paper is developed, we shall have the temperature indicated by the thermometer at any given period. Thus in Fig. 15 we

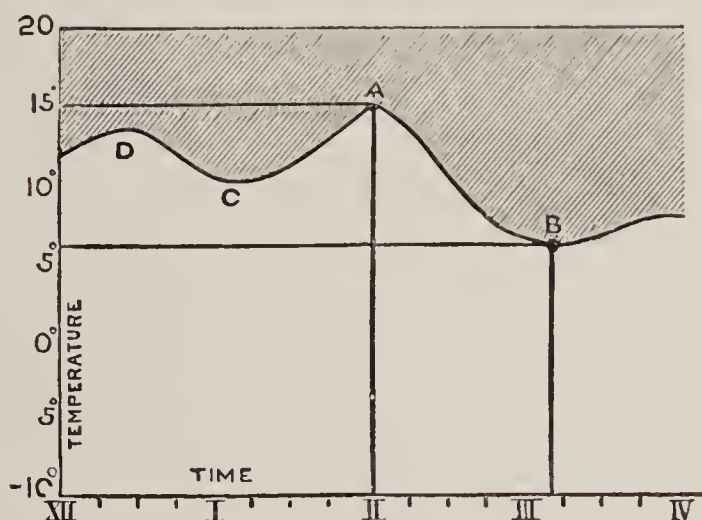


FIG. 15.

see that the maximum temperature (point A) was 15.2° C. at two o'clock, the minimum (point B) was 6° at nine minutes past three. Maximum and minimum positions are also indicated at D and C, and the temperature at any particular time is known. The information is much more definite than that given by the ordinary forms.

For special purposes (deep-sea soundings, medical, etc.) special thermometers have been designed. Particulars of

thermometers (pyrometers) for registering very high temperatures will be given in a later chapter (see Index).

13. Differential Thermometer.—This thermometer, constructed first by Leslie, measures differences of temperature. The modified form shown in Fig. 16 is easily constructed.

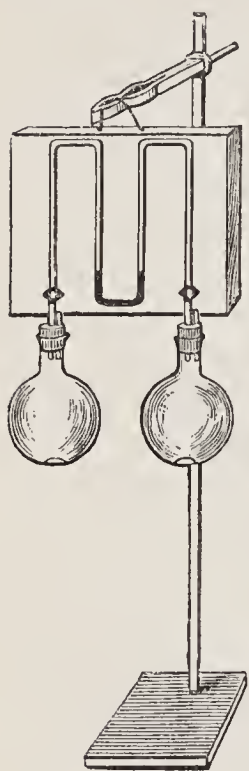


FIG. 16.

Two 2-oz. flasks, fitted with good indiarubber corks, are connected by a piece of thin glass tubing 24 inches long, bent as in Fig. 16. A coloured liquid is drawn into the bend; this liquid can be adjusted by the aid of a stopper in each cork so that it stands at the same height in each limb. The whole is fastened to a board. It can, if necessary, be adjusted by placing each flask in a bath of water, one bath being 5° higher in temperature than the other. The distance between the two heights of the liquid in each limb is divided into five equal parts. The instrument is used generally to indicate differences of temperature, and therefore need not be graduated.

14. Mercury as a Thermometric Substance.—Mercury is selected for thermometers for the following reasons:—

- (1) It can be obtained pure.
- (2) Its expansion is almost regular for all ordinary temperatures.
- (3) It freezes at -40° C. and boils at 350° C., and is therefore a liquid at all ordinary temperatures.
- (4) It is a good conductor, and therefore the whole of the mercury soon attains the temperature of any enclosure.

(5) It acts quickly (§ 2), and requires but a small quantity of heat to raise its temperature; that is, its specific heat is small.

15. Testing Thermometers.—The class thermometers should be tested. An ordinary tin with a few holes punched in the bottom, and filled with *clean ice*, will serve for testing the freezing point. Afterwards mix salt with the ice, and test again, and note the effect of impurities.

For verifying the boiling point, a flask with a long neck

and half filled with clean water may be used (Fig. 17). Pass a thermometer through a cork, through which also passes a bent open tube; the thermometer must not touch the water; it should be merely surrounded with steam. (What are the defects of this arrangement? Compare Figs. 7 and 8.)

Add salt to the water, and again notice the height of the mercury when the thermometer is immersed in the steam. Place the thermometer in the salt and water, and again observe the temperature. Try mixtures of calcium chloride and water.

To observe the influence of pressure, connect the tubes of A and B. The tube B dips into water, and therefore the pressure inside the flask is greater than that of the atmosphere. Replace the water in C with mercury, and test again.

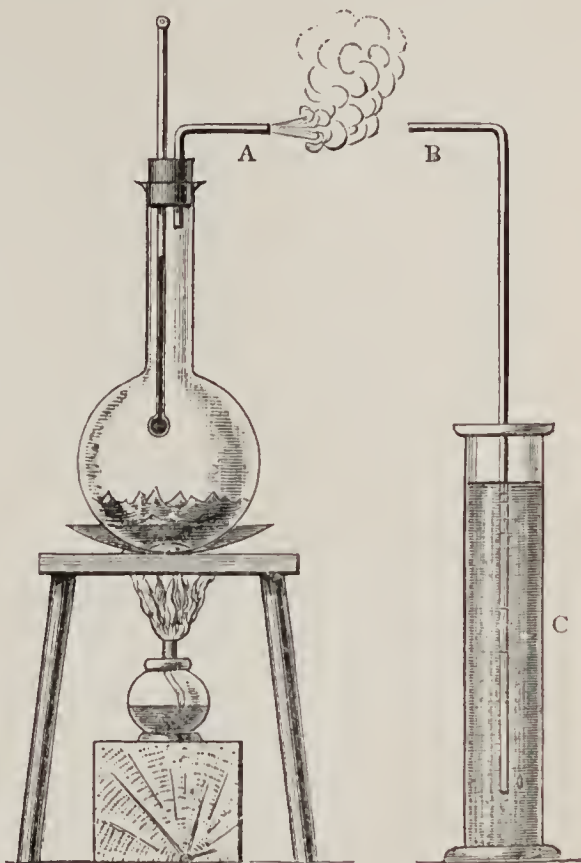


FIG. 17.

EXAMPLES. I.

1. Define "heat" and "temperature."
2. Describe the construction of a mercurial thermometer. How are the fixed points determined?
3. What are the advantages and disadvantages of mercury over water as a thermometric substance, say between 10°C. and 40°C. ?
4. Change the following readings on the Centigrade scale into readings on a Fahrenheit and Reaumur scale: 100° , 0° , -273° , -38° , 200° .
5. The following readings are from a Fahrenheit thermometer: what will they be on a Centigrade thermometer: 212° , 32° , -32° , -460° ?
6. Why is steam used rather than water in determining the upper fixed point?
7. A thermometer with a uniform tube has 12 F. divisions in an inch, how many C. divisions would there be in an inch?

8. You test a cheap thermometer (C.), and find that the true freezing point is $+1^{\circ}$, and the true boiling point is 101° : what is the real value of 50° on such a thermometer?

9. A thermometer whose bulb alone is immersed in a liquid reads 44° F. Is this too high or too low—give reasons for your answer—in two cases, (a) when the temperature of the air is 60° F.; (b) when it is 32° F.?

10. A thermometer tube is given to you closed in the usual way, but without any markings: how would you determine the fixed points, and what plan would you follow in calibrating the tube?

CHAPTER II.

EXPANSION OF SOLIDS.

16. Coefficient of Linear Expansion.—The general effect that solids as a rule expand when their temperature is raised, and contract when their temperature falls, has already been referred to.

When we consider the change in length, as in estimating the expansion of a rod or of a telegraph line, we deal with linear expansion; if change of area is noted, we deal with areal or square expansion; and in change of volume we deal with cubical expansion.

If a body be perfectly isotropic, the change in length in any direction will be the same; in crystalline bodies the change in different directions will, in general, be different.

The coefficient of linear expansion for 1° is the ratio of the increase in length when the temperature is raised 1° to the original length.

Thus if a bar of iron be 4 feet long at 10°C. , and 4 feet 0.0472 inch at 100°C. , the increase in length is 0.00393 foot for 90° , and 0.0000433 foot for 1° . Therefore its coefficient of expansion for 1° is $0.0000433 \div 4$, or 0.000011 nearly.

This definition would be sufficient if the coefficient were the same for a given substance when measured at any temperature. Measurable differences, however, occur, so that the more correct definition is—

The coefficient of linear expansion at any given temperature is the ratio of the increase of length when the temperature is raised one degree to the original length at the given temperature.

In the Centigrade scale the coefficient is frequently defined so that the given temperature is 0° ; in the Fahrenheit scale it is frequently defined at 60° .

Ordinarily, the coefficient is deduced from experiments where the range of temperature is 100° or more, and the coefficient is determined by dividing the ratio by 100 or the number of degrees; that is, it is assumed that the coefficient of expansion is the same at all temperatures.

17. Lavoisier and Laplace's Method.—A brass trough rests upon a surface between four stone supports (Figs. 18 and

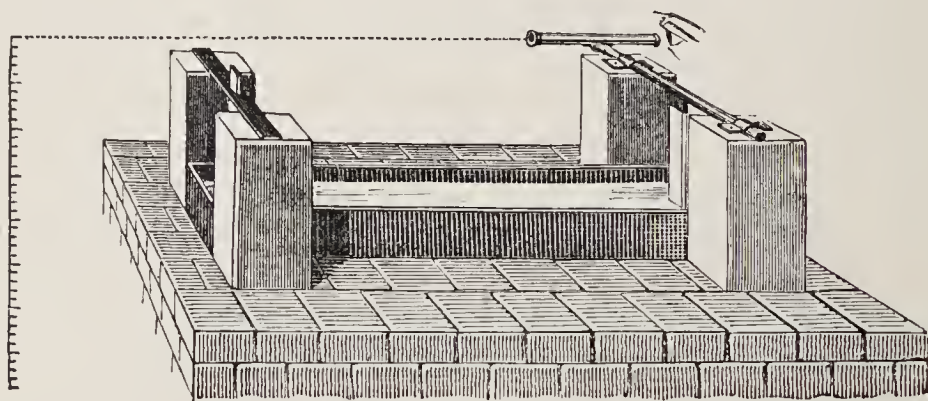


FIG. 18.

19). On two of the supports is an axis, carrying firmly a telescope, G; a glass rod, D, is securely fixed to the middle of the axis, at right angles to it. Both rod and telescope move with the axis. The other two supports also carry a bar, to which a glass rod, F, is fixed at right angles. This rod is kept firmly in its place by a stop.

The bar K H, whose expansion is to be measured, is placed on glass rollers in the trough, one end being firmly fixed against

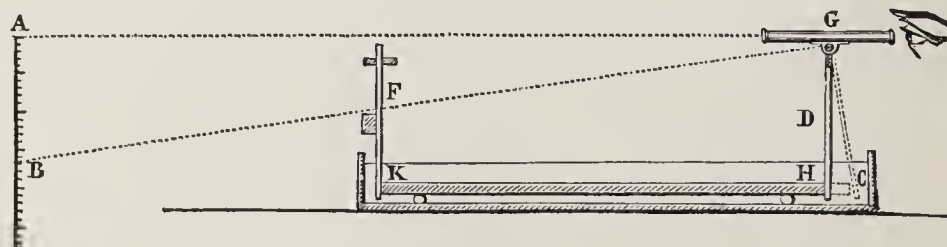


FIG. 19.

the glass rod F. The trough is first filled with melting ice, and the telescope, which is fitted with the ordinary cross-wires, is

directed towards a distant scale and the reading A is taken, care being taken that the glass rod D presses against the end H. The ice is removed, and the trough filled with oil or water, which is heated. The bar expands. The end K being fixed, the movement is registered by the end H, which moves to C, moves the rod D, and thus depresses the telescope, and the distant scale is again read at B.

At the beginning of the experiment it was arranged so that the angles BAG and GHC were right angles. The angle AGB = angle HGC. Therefore the triangles AGB and HGC are similar.

$$\therefore \frac{HC}{AB} = \frac{GH}{AG}$$

GH and AG were carefully measured at the beginning, and were constant for each experiment. In a series $\frac{GH}{AG} = \frac{1}{744}$

$$\therefore HC = \frac{AB}{744}$$

AB is read off on the scale.

On dividing HC by the original length of the bar, and by the number of degrees through which the bath is heated, we obtain the coefficient of expansion.

The difficulty consists in determining exactly where the bar touches G H, and measuring from this point to the optical axis of the telescope. More satisfactory results are obtained when the elongation is measured by means of a micrometer screw. If a screw is made with say a hundred turns to the inch, and works in a fixed socket, then each turn of the head indicates that the screw has moved forward a distance of 0.01 inch; if the circumference of the head of the screw be divided into a hundred parts, then, if the head be turned through one division, a distance is indicated of 0.0001 inch. The accuracy of the instrument depends upon its construction.

18. Roy and Ramsden's Method.—The following is a modification of Roy and Ramsden's method: Two bars of equal lengths of cast iron are placed in two troughs, A and C (Fig. 20). The bars, each about 6 feet long, are surrounded

with melting ice. Vertical rods are fixed at the ends of these bars; on the rods in one bar are placed two telescopes with the usual cross-wires; on those of the other bar are two cross-wires suitably illuminated.

The centres of the cross-wires and the optical axes of the eye-pieces are a known equal distance apart, a distance that

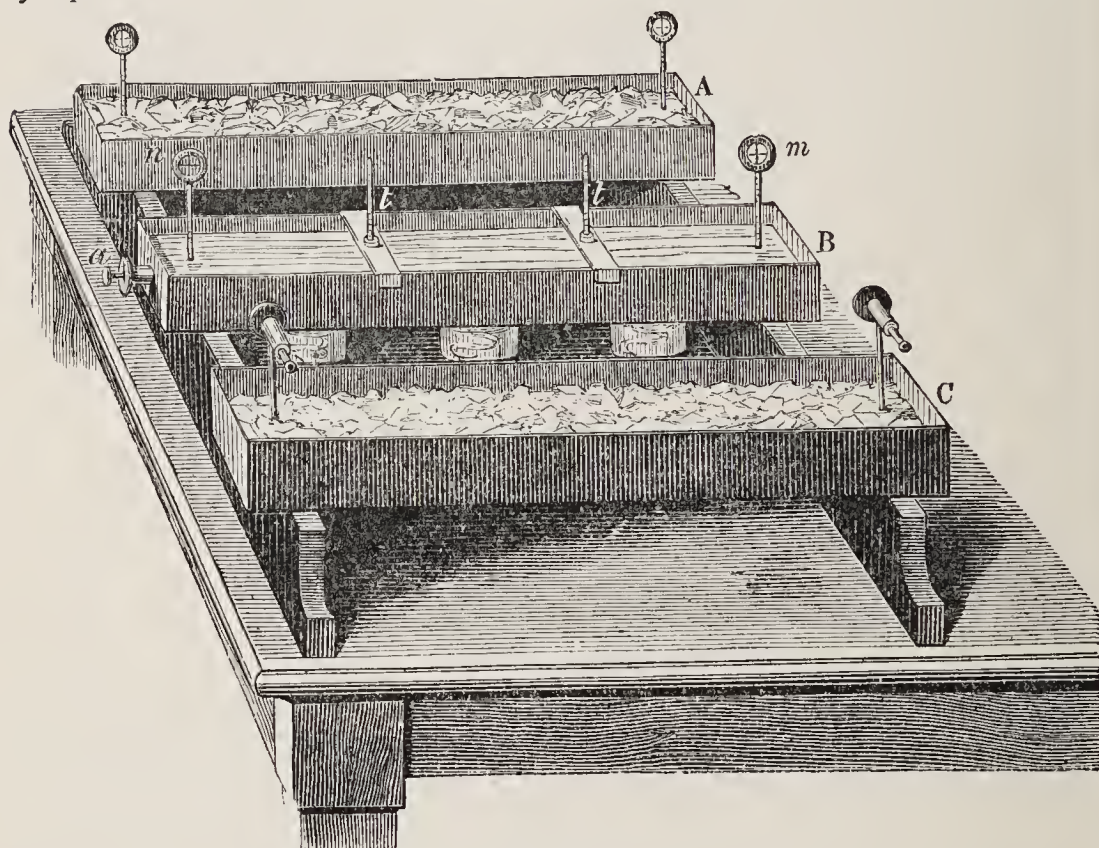


FIG. 20.

remains constant during the experiment, seeing that the bars remain at freezing point. Between these troughs is a third trough, B, containing the bar whose elongation is to be measured. It carries similar vertical rods, each carrying cross-wires, n and m . The cross-wire n is movable, by means of a micrometer screw, along the axis of its bar. The middle bar is surrounded with melting ice, and the apparatus is arranged so that, on looking through the telescopes of C, the cross-wires in A and B are clearly seen one behind the other. Under these conditions the distance between the intersections of the cross-wires in B is the known distance between the centres of the cross-wires in A or the centres of the cross-wires in the telescopes. The trough B is now heated to the temperature of boiling water

or boiling oil, the exact temperature being indicated by the thermometers t, t . The end of the rod near m is kept fixed, so that all the elongation is effected at n . The agreement between the cross-wires is now disturbed, the micrometer screw a is turned, and the turns and parts of a turn noted necessary to bring the cross-wire n into agreement again. This measures the elongation, and the coefficient of expansion can be calculated.

19. Direct Method.—The following method is described in Glazebrooke and Shaw's "Practical Physics." Its advantage is that the measurements are taken direct.

The reading microscopes described stand vertically, and, by turning a micrometer screw, move horizontally. The movement is registered by an index moving along a scale divided into millimetres, the distance between two threads of the screw is also 1 mm., so that each complete turn of the screw moves the microscope one millimetre. The head of the screw is divided into 100 parts, therefore moving it through one part moves the microscope, and therefore the index, through $1 \text{ mm.} \times \frac{1}{100} = 0.01 \text{ mm.}$ The apparatus is so constructed that when the zero of the screw is at the mark, the index is on one of the divisions.

If the index on one microscope be between the forty-fifth and forty-sixth divisions, and the screw-head denotes 76, then the position denoted is 45.76 mm., or 4.576 cm.

"We require to measure the length of a rod, or the distance between two marks on it, at two known temperatures, say 15° C. and 100° C.

"The highest degree of accuracy requires complicated apparatus. The following method is simple, and will give very fair results:—

"A thick straight rod is taken, about 50 cm. in length, and a glass tube of 4 or 5 cm. bore and somewhat greater length than the rod. The tube is closed with a cork at each end, and through each cork a small piece of glass tubing is passed, and also a thermometer. Two fine scratches are made on the rod, one close to each end, at right angles to its length, and

two other scratches, one across each of the former, parallel to the length. The glass tube is clamped in a horizontal position and the rod placed inside it, resting on two pieces of cork or wood in such a manner that the scratches are on the upper surface and can be seen through the glass. The whole should rest on a large stone slab—a stone window-sill serves admirably.

“The piece of glass tubing in one of the corks is connected with a boiler from which steam can be passed into the tube; the other communicates with an arrangement for condensing the waste steam.

“A pair of reading microscopes are then brought to view the cross-marks on the rod, and are clamped securely to the stone. The microscopes should be placed so that they slide parallel to the length of the rod; this can be done by eye with sufficient accuracy for the purpose.

“For convenience of focussing on the rod which is in the glass tube, the microscopes must not be of too high a power. Their supports should be clamped down to the stone at points directly behind or in front of the position of the microscopes themselves, to avoid the error due to the expansion of the metal slides of the microscopes, owing to change of temperature during the experiment.

“Call the microscopes A and B; let A be the left-hand one of the two, and suppose the scale reads from left to right. Turn each microscope tube round its axis until one of the cross-wires in the eye-piece is at right angles to the length of the rod, and set the microscope by means of the screw until this cross-wire passes through the centre of the cross on the rod.

“Read the temperature, and the scale and screw-head of each microscope, repeating several times. Let the mean result of the readings be—

Temperature.	A	B
15° C. ...	5.106 cm. ...	4.738 cm.

“Now allow the steam to pass through for some time; the marks on the copper rod will appear to move under the microscopes, and after a time will come to rest again.

“Follow them with the cross-wires of the microscopes, and read again. Let the mean of the readings be—

Temperature.	A	B
100° C. ...	5.074 cm. ...	4.780 cm.

“Then the length of the rod has apparently increased by $5.106 - 5.074 + 4.78 - 4.738$, or 0.074 cm.

“The steam will condense on the glass of the tube which surrounds the rod, and a drop may form just over the cross and hide it from view. If this be the case, heat from a small spirit-flame or Bunsen burner must be applied to the glass in the neighbourhood of the drop, thus raising the temperature locally and causing evaporation there.

“Of course, the heating of the rod and tube produces some alteration in the temperature of the stone slab, and causes it to expand slightly, thus producing error. This will be very slight, and for our purpose negligible, for the rise of temperature will be small and the coefficient of expansion of the stone is also small.

“We have thus obtained the increase of length of the rod due to the rise of temperature of 85° . We require also its original length.

“To find this remove the rod and tube and replace them by a scale of centimetres, bringing it into focus. Bring the cross-wires over two divisions of the scale, say 10 and 60, and let the readings be—

A	B
4.576 cm. ...	5.213 cm.

Then clearly the length of the rod at 15° C. is—

$$50 - (5.106 - 4.576) + (4.738 - 5.213), \text{ or } 48.995 \text{ cm.}$$

“To find the coefficient of expansion, we require to know the length at 0° C. This will differ so little from the above that we may use either with all the accuracy we need, and the

required coefficient is $\frac{0.074}{85 \times 48.995}$, or 0.0000178 .

“*Experiment.*—Determine the coefficient of expansion of the given rod.

“Enter results thus—

Increase of length of rod between 15° and 100° C.	0.074 cm.
Length at 15°	48.995 cm.
Coefficient	0.0000178”

(See Worked Examples, p. 32, No. 2.)

20. Exceptions.—Generally bodies expand when heated. Stretched indiarubber, iodide of silver, and a few other substances contract when their temperature is raised. Their coefficient of expansion is negative. If a tube of indiarubber be slightly stretched, and steam be passed through, the contraction can be readily observed; if the indiarubber be suddenly stretched, its temperature rises.

21. Results.—The coefficients of linear expansion are small quantities, and can only apply to the particular specimens experimented upon. The coefficient will vary, for example, with particular specimens of iron, and the numbers, as will have been seen by the experiments, are generally calculated by measuring the expansion for 100° , and thus measure the average expansion between two given temperatures.

TABLE OF COEFFICIENTS OF LINEAR EXPANSION FOR 1° C.

Glass ... = 0.0000085	Copper ... = 0.000017
Platinum ... = 0.0000085	Brass ... = 0.000019
Steel ... = 0.000012	Silver ... = 0.000019
Cast iron ... = 0.000011	Tin ... = 0.000022
Wrought iron = 0.000012	Lead ... = 0.000029
Gold ... = 0.000015	Zinc ... = 0.000029

The values for the Fahrenheit scale will be $\frac{5}{9}$ of these for the Centigrade scale.

22. Practical Applications.—The change in length due to change of temperature in solid bodies is exceedingly small, and in practice may generally be neglected. For exact purposes, such as determining the standard measures, it must be observed.

The standard yard is defined as the distance between the centres of the transverse lines in the two gold plugs in the bronze bar deposited in the office of the Exchequer at 62° F.

In the case of the French metre, the length is to be taken at the temperature of melting ice.

In bridges, as has already been observed, the expansion must be allowed for; not only do the substances expand or contract, but they do work in so doing. An iron rod, for example, 1 square inch in section, in cooling through $9^{\circ}\text{C}.$, would exert a force of 1 ton. The force of contraction is illustrated in Fig. 21. An iron bar, A B, passes through

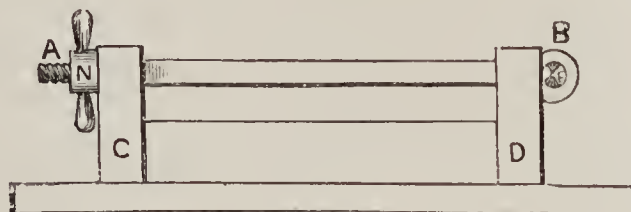


FIG. 21.

sockets in a strong cast-iron frame, C D. The iron bar has a hole in one end, B, through which passes a cast-iron rod, F; at the other end is a screw-thread, on which a nut, N, with two arms, works. The rod is heated, placed in the sockets; the rod F is inserted, and the nut screwed up tightly. As the temperature falls, the bar contracts, and the force is sufficient to break the small bar F.

By passing iron bars through buildings, fixing screws to the ends, and tightening these screws when the bars are heated, it has been possible to straighten walls that have bulged out; the force exerted on cooling being sufficient to gradually bring the walls to their original position.

A striking illustration is afforded in the case of telegraph wires. An iron wire stretched across a span of 400 feet, with a "sag" of 5 feet at the temperature $25^{\circ}\text{C}.$, would have a strain upon it of 13,544 lbs. per square inch. In winter, at a temperature of $-5^{\circ}\text{C}.$, the strain would be 34,000 lbs. per square inch, sufficient to permanently stretch the wire.

The effect of change of temperature on the strength of materials is important in practical work, especially in the construction of boilers. Cast iron, for example, loses strength when heated above $120^{\circ}\text{F}.$; wrought iron seems constant up to $400^{\circ}\text{F}.$, it then declines, until at red heat its strength has fallen from 20 tons to $15\frac{1}{2}$ tons per square inch.

23. Compensating Pendulums.—The number of swings made by the pendulum of a clock in a given time varies inversely as the square root of the length of the pendulum. It is therefore necessary to devise methods to keep the length of the pendulum constant during changes of temperature. In Harrison's gridiron pendulum (Fig. 22) the bob is supported by framework, as in the figure. The five shaded portions (d, e, i, \dots , and the piece b) are steel; the others (c, n, \dots) are brass. An examination of the figure shows that the steel (fixed at the top), expanding, will lower the bob, while the expansion of the brass (fixed at the bottom) will lift the bob.

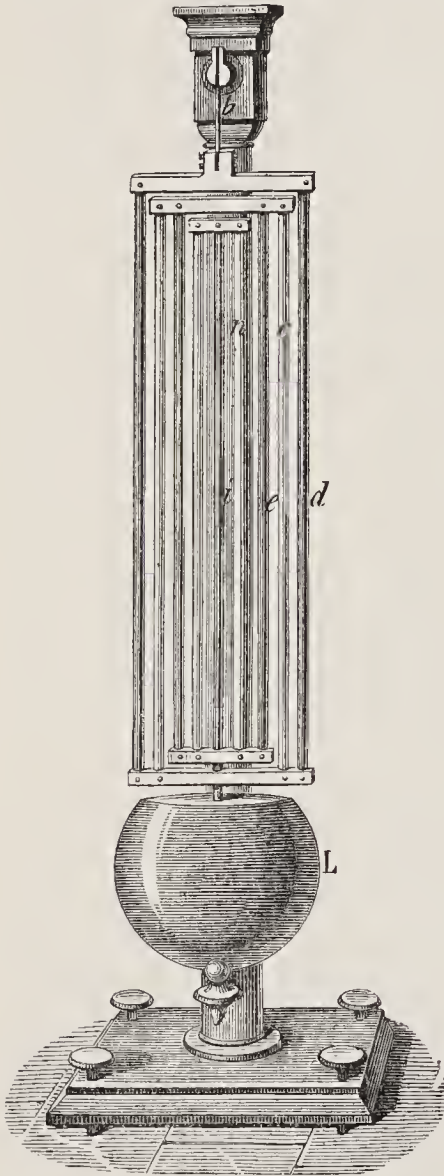


FIG. 22.

From the Table, p. 26, the coefficients of expansion of steel and brass are as 12 : 19. Then evidently the lengths of steel and brass must be inversely as these numbers; that is, $\frac{b + i + e + d}{n + c} = \frac{19}{12}$.

So constructed, the distance of the centre of the "bob" from the point of suspension will be constant at all temperatures. It is, perhaps, needless to say that most of the compensating pendulums in

ordinary clocks are mere toys.

If strips of brass and zinc be soldered together, and be then heated, the strip bends. The coefficients of expansion of brass and zinc are as 19 : 29; therefore, in expanding, the zinc forms the convex side of the compound bar.

Advantage is taken of this in constructing the balance-wheels of chronometers.

The rate of a chronometer depends upon the mass of the

balance-wheel and the distance of the circumference from the centre. The parts B, C (Fig. 23) are made up of a compound strip, the metal with the highest coefficient being on the outside. When the temperature rises, the radius A expands, and the chronometer would lose time, but the heat causes the strips B, C to curve inwards. The masses D are thus brought nearer the centre, and this compensates for the expansion of A.

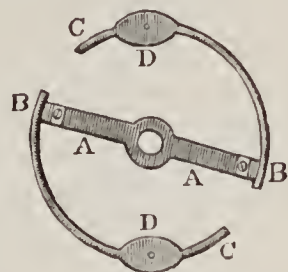


FIG. 23.

24. Coefficient of Square Expansion.—The coefficient of square expansion is the ratio of the increase in area for one degree to the original area.

If a square of unit side expands for one degree so that the side becomes $(1 + k)$, k being numerically equal to the coefficient of linear expansion, the area, if the body be isotropic, will be $(1 + k)^2$, and the coefficient of expansion for square expansion will be $\frac{2k + k^2}{1}$. But k being small, k^2 can be neglected, and we have the coefficient of areal expansion = $2k$; *i.e.* twice the coefficient of linear expansion. If the coefficient of expansion in one direction be k_1 , in the other k_2 , then the new area = $(1 + k_1)(1 + k_2) = 1 + k_1 + k_2 + k_1k_2$. k_1k_2 can be neglected, and the coefficient equals $\frac{k_1 + k_2}{1}$ = $k_1 + k_2$, the sum of the coefficients of linear expansion.

An examination of the Table, p. 26, shows that the linear expansions, and therefore the areal and cubical expansions, of glass and platinum are equal. It is this fact that makes it possible for platinum wire to be fused into glass. If the expansion (areal) were greater, then, on cooling, either the glass would crack or the tube would not be air-tight.

25. The Coefficient of Cubical Expansion is the ratio of the increase in volume for one degree to the original volume.

If the body be isotropic, then a cube whose side is unity will have a side $1 + k$ when the temperature rises 1° . Therefore the new volume = $1 + 3k + 3k^2 + k^3$. k^3 and similarly k^2

are very small compared with k , and may be neglected, so that the coefficient of cubical expansion $= \frac{3k}{1} = 3k$; *i.e.* three times the coefficient of linear expansion. Imagine the cube with thick

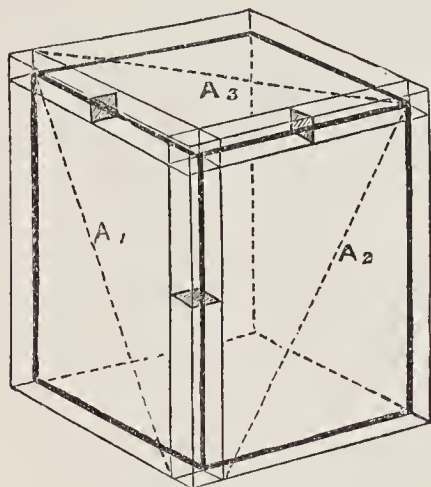


FIG. 24.

lines to be 1 foot each side (Fig. 24). After expansion the complete cube is formed, made up as regards volume, of the original cube + 3 square slabs (A_1, A_2, A_3 are the diagonals; volume of each is $1 \times 1 \times d$) + 3 strips (a section of each is shown; volume of each is $1 \times d \times d$) + a small cube whose volume is $d \times d \times d$. This illustrates that $(1 + k)^3 = 1 + 3k + 3k^2 + k^3$. We are able to neglect k^3 and k^2 , because

they are so small compared with k . For solid bodies k is less than 0.00003, so that for a change of 100° we should have $3k^2$ less than 0.00000027, or $\frac{1}{3700000}$ of the total.

If, therefore, the solid be isotropic, or, being crystalline, if its coefficients of linear expansion be the same in all directions, the coefficient of cubical expansion can be calculated from the coefficient of linear expansion.

In many crystals the coefficients of expansion in the direction of three axes are not equal; the result of increase of temperature is therefore distortion of shape. The coefficient of cubical expansion is in these cases the sum of the three coefficients.

26. Small Quantities.—The coefficient of expansion numerically equal to the expansion of unit length when the temperature is raised one degree *is small compared with unity*, and therefore the second and third powers can generally be neglected. This has already been shown to be the case for solids. The same powers can generally be neglected in liquids. In gases we shall see the coefficient is generally about the value 0.003665 (compare this with 0.00003); the degree of accuracy required must determine, in questions relating to gases, the powers that may be disregarded.

Generally let d , e , and f be quantities small compared with unity.

Approximation to the		
	First order of small quantities.	Second order of small quantities.
$(1+d)^2 = 1 + 2d + d^2$	$1 + 2d$	$1 + 2d + d^2$
$(1-d)^2 = 1 - 2d + d^2$	$1 - 2d$	$1 - 2d + d^2$
$(1+d)(1+e) = 1 + d + e + de$	$1 + d + e$	$1 + d + e + de$
$(1+d)^3 = 1 + 3d + 3d^2 + d^3$	$1 + 3d$	$1 + 3d + 3d^2$
$(1-d)^3 = 1 - 3d + 3d^2 - d^3$	$1 - 3d$	$1 - 3d + 3d^2$
$(1+d)(1+e)(1+f) = 1 + d + e + f + de + df + ef + def$	$1 + d + e + f$	$1 + d + e + f + de + df + ef$
$\frac{1}{1+d} = 1 - d + d^2 - d^3 + \text{etc.}$	$1 - d$	$1 - d + d^2$
$\frac{1}{1-d} = 1 + d + d^2 + d^3 + \text{etc.}$	$1 + d$	$1 + d + d^2$
$\frac{1+d}{1+e} = 1 + d - e - de + e^2 + \text{etc.}$	$1 + d - e$	$1 + d - e - de + e^2$

27. Density and Temperature.—If L_0 be the length of a bar at 0° , and k be the coefficient of linear expansion, then at t° the length is $L_0(1 + kt)$, and

$$L_t = L_0(1 + kt)$$

If V represent volume—

$$V_t = V_0(1 + 3kt)$$

The density of any substance at any temperature is the mass of unit volume at that temperature.

If V_0 , V_t , V_T be the volumes of a substance at 0° , t° , and T° , and D_0 , D_t , D_T be the densities of the substance at 0° , t° , and T° , the mass of the substance is the product of volume and density, and, of course, does not change with expansion.

$$\therefore \text{mass} = M = V_0 D_0 = V_t D_t = V_T D_T$$

That is—

$$V_t : V_T :: D_T : D_t$$

or the densities are inversely as the volumes. If K = coefficient of cubical expansion—

$$V_t = V_0(1 + Kt)$$

$$\therefore D_T : D_t = 1 + Kt : 1 + KT$$

$$\therefore D_T = D_t \frac{1 + Kt}{1 + KT} = D_t[1 + K(t - T)]$$

if K be small compared with unity. In the special case where $t = 0$ —

$$D_T = D_0 \frac{1}{1 + KT} = D_0(1 - KT)$$

if K be small compared with unity.

WORKED EXAMPLES.

1. A rod of copper measures 10 feet at 0°C .; its length at 100°C . is 10 feet 0.191 inch: find the coefficient of expansion of copper.

$$\begin{aligned} \text{The increase in length for } 100^\circ &= 0.191 \text{ inch} = 0.0159 \text{ foot} \\ \text{,, ,, } 1^\circ &= 0.000159 \text{ foot} \\ \therefore \text{coefficient} &= \frac{\text{increase in length for } 1^\circ}{\text{original length}} = \frac{0.000159 \text{ ft.}}{10 \text{ ft.}} = 0.0000159 \\ &= 0.000016 \text{ nearly} \end{aligned}$$

2. See example at the end of § 19.

The result obtained is the mean coefficient between 15° and 100° (the correct integers are 17769). We might consider it more accurately thus: If k be the coefficient of linear expansion—

$$\begin{aligned} L_{15} &= L_0(1 + 15k) & L_{100} &= L_0(1 + 100k) \\ \therefore \frac{L_{100}}{L_{15}} &= \frac{49.069}{48.995} = \frac{1 + 100k}{1 + 15k} & (A) \end{aligned}$$

$$\begin{aligned} \therefore 49.069 + 15 \times 49.069k &= 48.995 + 4899.5k \\ \therefore k(4899.5 - 1736.035) &= 0.074 \end{aligned}$$

$$\therefore k = \frac{0.074}{4163.415} = 0.000017774$$

Now, obviously the errors of the experiment are greater than any meaning we can attach to figures in the seventh and eighth places; there is thus no advantage in the latter method. If at step A we write $\frac{1 + 100k}{1 + 15k} = 1 + k(100 - 15) = 1 + 85k$, then $k = \frac{1}{85} \left(\frac{49.069}{48.995} - 1 \right) = \frac{0.074}{85 \times 48.995}$ *i.e.* the result by the approximate method.

3. A rod is measured at 75°F .; by the brass scale used its length is 18.04 inches; the scale was, however, graduated at the temperature of melting ice, and its mean coefficient of expansion between melting point

and freezing point is 0.0000105 per degree Fahrenheit: find the real length of the rod.

The brass scale has expanded, and therefore indicates too low a measurement.

1" on the scale at 32° F. measures $(1 + 0.0000105 \times 43)" = 1.0004515"$ at 75° F.

$$\therefore \text{the true length of 1" at } 75^{\circ} \text{ F. is } \frac{1}{1.0004515} \text{ inch}$$

$$\therefore \text{the true length of the rod} = 18.04 \frac{1}{1.0004515} = 18.032 \text{ inches}$$

practically a negligible quantity.

4. The volume of a leaden ball at 60° F. is 100 cubic inches: find its volume at the boiling point of water (mean coefficient of linear expansion on the Fahrenheit scale, 0.0000157).

$$\text{Coefficient of cubical expansion (K)} = 0.0000471$$

$$\begin{aligned} \therefore V_{212} &= V_{60}(1 + 152 \times 0.0000471) \\ &= 100(1.0071592) \\ &= 100.716 \text{ cubic inches} \end{aligned}$$

EXAMPLES. II.

1. Three rods of glass, copper, and silver, are each 10 feet long at 0° C.: find their lengths at 100° C.

2. The coefficient of linear expansion for a specimen of English flint glass was found to be 0.00000451 per degree Fahrenheit: compare the density of such glass at 32° F. and at 212° F.

3. The diameter of a tin sphere at 15° C. is 10 cm.: find its volume at 85° C.

4. One end of a cast-iron girder in a factory is fixed: what play must be allowed the other end when the range of temperature to which it is subjected is between 20° F. and 250° F. (the length of the girder is 25 feet)?

5. Two pendulums, one of brass, the other of iron, beat seconds when the temperature is 15° C.: compare the number of beats made per day by each, (a) when the temperature is 25° C.; (b) when it is -10° C.

6. In an experiment illustrating Lavoisier and Laplace's method, the ratio of $\frac{GH}{AG} = \frac{1}{100}$, and 100 divisions of this scale equal 18 inches.

The bar H K is copper and is 1 yard long at 0° C. When the bath is filled with boiling water whose temperature is 100° , the distance A B is found to be 35 divisions. Find the expansion of copper.

7. The density of gold at 0° C. is 19.211 , at 100° C. it is 19.129 : find the mean coefficient of cubical and linear expansion of this metal.

CHAPTER III.

EXPANSION OF LIQUIDS.

28. Apparent and Absolute Expansion.—In measuring the expansion of liquids we have to consider the expansion of the glass envelope, and ordinarily we measure the apparent expansion of the liquid. The student should repeat the experiment in § 2 (Liquids).

The expansion of glass makes the apparent increase in volume less than the real increase in volume of the liquid (§ 2).

The coefficient of apparent expansion of a liquid in a given envelope at a given temperature, is the ratio of the apparent increase in volume for one degree to the original volume.

The coefficient of absolute expansion at any temperature, is the ratio of the absolute increase in volume for one degree to the original volume.

Let Δ be the true dilatation of a liquid for a given range of temperature; D , the apparent dilatation; G , the dilatation of the envelope; V , the original volume. After heating through a given range of temperature, since D is the apparent dilatation, the apparent volume is $V(1 + D)$. But since the envelope has dilated, the true volume of every apparent unit of volume is $(1 + G)$; \therefore the true volume of that which is apparently $V(1 + D)$ is $V(1 + D)(1 + G)$. But this equals $V(1 + \Delta)$, since Δ is the true dilatation.

$$\therefore V(1 + \Delta) = V(1 + D)(1 + G)$$

$$\therefore (1 + \Delta) = (1 + D)(1 + G)$$

$$\therefore \Delta = D + G + DG$$

The whole of these quantities are very small, and the product DG can be neglected, compared with Δ , D , or G .

$$\therefore \Delta = D + G$$

That is, the real increase practically equals the apparent increase together with the increase in volume due to the expansion of the glass. If the increase of temperature be t° , we have—

The coefficient of absolute expansion of a liquid equals the apparent expansion of the liquid together with the coefficient of cubical expansion of the glass enclosing the liquid.

29. Weight Thermometer.—The apparent expansion of a liquid can be determined by a weight thermometer.

A glass tube about 6 inches long, with an internal diameter of $\frac{1}{2}$ inch, is closed at one end; the other end finely drawn out is made into the shape of Fig. 25, and is left open.

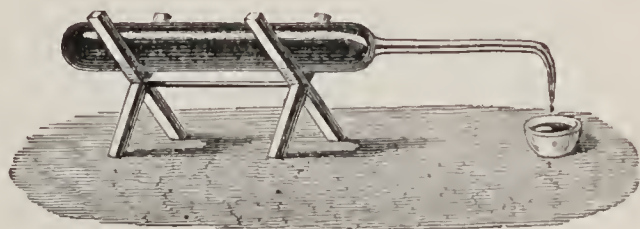


FIG. 25.

The apparatus is weighed, and is then rested upon a convenient support, with the open end dipping into mercury. The bulb is warmed. On cooling, mercury is forced into it; the process is repeated until the thermometer is completely filled (the process of filling a thermometer is followed). The whole is allowed to cool to the temperature of the room, the point dipping into mercury. Any adhering particles being brushed away, it is weighed, and the temperature is taken. Subtracting the weight of the glass, we obtain the weight of mercury in the thermometer at t° .

The thermometer is now placed in a wire cage, care being taken that no mercury escapes, and put into a steam bath. The mercury forced out as the temperature rises is caught in a weighed capsule. When no more mercury escapes, and the temperature is steady, the temperature of the bath is read, and the weight thermometer removed. It is allowed to cool

to the temperature of the room, and is then weighed again. The method of working will be best seen from an example.

$$\text{Tube + mercury at } 15^{\circ} = 192.3 \text{ grams}$$

$$\text{Empty tube} = \underline{15.6} \quad ,,$$

$$\therefore \text{weight of mercury} = \underline{176.7} \quad ,,$$

$$\text{Tube + mercury at } 100^{\circ} = 190.0 \quad ,,$$

$$\text{Tube} = \underline{15.6} \quad ,,$$

$$\therefore \text{weight of mercury} = \underline{174.4} \quad ,,$$

174.4 grams of mercury at 15° expand so as to occupy at 100° the volume of 176.7 grams at 15° .

$$\therefore \text{expansion for 1 gram} = \frac{176.7 - 174.4}{174.4} = \frac{2.3}{174.4}$$

\therefore coefficient of apparent expansion of mercury in glass

$$= \frac{2.3}{174(100 - 15)} = 0.000153$$

In this particular weight thermometer 2.3 grams are expelled when the temperature rises 85° ; that is, 0.027 gram is expelled when the temperature rises 1° . If, then, the thermometer be filled when the temperature of the room is, say, 16° , and it be then placed in an enclosure at a higher temperature, and we collect the mercury expelled—let us say 1.8 gram—then the temperature of the enclosure is $\frac{1.8}{.027}$ degrees above the room; that is, the temperature is $(16 + 66.7)^{\circ} = 82.7^{\circ} \text{C}$. The origin of the name “weight thermometer” is now seen. (See also Example 1, p. 55.)

In a general example, let the thermometer be first weighed at 0°C .

Let V_0 = volume of the thermometer at zero.

D_0 = density of mercury at zero.

M = mass of mercury that fills the thermometer at 0°C .

m = mass of mercury expelled when the thermometer is heated to t° .

The apparatus at t° contains a mass, $M - m$. \therefore the volume of this mass at zero $= \frac{M - m}{D_0}$ (since $M = V \times D$). (§ 27.)

The real volume of this mercury at $t^\circ = \frac{M - m}{D_0}(1 + \Delta t)$, where Δ is the coefficient of absolute expansion of mercury.

The thermometer at 0° contains a mass of mercury, M , \therefore its volume and also the volume of the glass at zero is $\frac{M}{D_0}$, and the volume of the glass at $t^\circ = \frac{M}{D_0}(1 + Kt)$, where K is the coefficient of cubical expansion of glass. This equals the real volume occupied by $M - m$ of the mercury at t°

$$\frac{M - m}{D_0}(1 + \Delta t) = \frac{M}{D_0}(1 + Kt)$$

Also, if d = coefficient of apparent expansion of mercury in glass—

$$(1 + \Delta t) = (1 + dt)(1 + Kt) \quad (\S 28.)$$

$$\therefore (M - m)(1 + dt) = M$$

$$\therefore d = \frac{m}{(M - m)t}$$

In order to use the instrument as a thermometer, a careful determination should be made between 0° C. and 100° C.; the amount expelled, m , divided by 100 (call this μ) will give the weight expelled for a rise of 1° . If in any other experiment n grams be expelled, then $\frac{n}{\mu}$ = the rise in temperature in degrees.

We assume that the expansion of mercury and glass is uniform from 0° C. to 100° C.; that is, the expansion for 1° is $\frac{1}{100}$ of the expansion from 0° to 100° C.

30. The Absolute Expansion of Mercury.—The results obtained by Dulong and Petit (§ 31) are given in the first column; the approximations of Regnault (whose method is given in § 32) are given in the second column. The student will notice that the coefficient increases with the temperature.

MEAN COEFFICIENTS OF THE ABSOLUTE EXPANSION OF MERCURY.

	Dulong and Petit.		Regnault.	
Between 0° and 100°	...	$\frac{1}{5550}$...	$\frac{1}{5508}$
„ 0° „ 200°	...	$\frac{1}{5425}$...	$\frac{1}{5425}$
„ 0° „ 300°	...	$\frac{1}{5300}$...	$\frac{1}{5360}$

The coefficient of apparent expansion of mercury in glass is generally given as $\frac{1}{6480}$, following Dulong and Petit. The fraction will vary with the kind of glass used, and should be determined for each instrument.

$$\begin{array}{ccc} (a) & (b) & (c) \\ \left. \begin{array}{l} \text{Coefficient of abso-} \\ \text{lute expansion of} \\ \text{mercury} \end{array} \right\} = & \left\{ \begin{array}{l} \text{Coefficient of appa-} \\ \text{rent expansion of} \\ \text{mercury} \end{array} \right\} + & \left\{ \begin{array}{l} \text{Coefficient of} \\ \text{cubical expan-} \\ \text{sion of glass.} \end{array} \right\} \end{array}$$

We can determine (b) (§ 29). If (a) were known, we have a ready method of calculating (c).

For example, taking Dulong and Petit's results, $(c) = \frac{1}{5550} - \frac{1}{6480} = \frac{1}{38700} = 0.0000258$. For ordinary chemical glass 0.0000254 is a better value.

These determined, we could substitute any other liquid, say glycerine or water, in the weight thermometer, by experiment find (b) for the liquid, then (c) being known, (a) for the liquid would be known.

The important matter is to find the coefficient of absolute expansion for some liquid by some independent method. Mercury, seeing that it can be obtained pure, that it does not at ordinary temperatures evaporate, and that it is used in many experiments, has been subjected to careful examination. The method is long, and demands special precautions; the principle, however, is readily grasped.

31. Dulong and Petit's Method.—If we take a U tube (Fig. 26), place it vertically, pour mercury sufficient to rise slightly in each limb, and then pour any liquid into one limb; then, if we draw a horizontal plane, B C, through the surface of separation, B, we know, by the hydrostatical principle, when all is in equilibrium, that the heights of the liquids above the surface of contact are in the inverse ratio of their densities. For example, if B C D be mercury, and B A water, B A in the tube n will be about $13\frac{1}{2}$ times the height of C D in the tube m ;

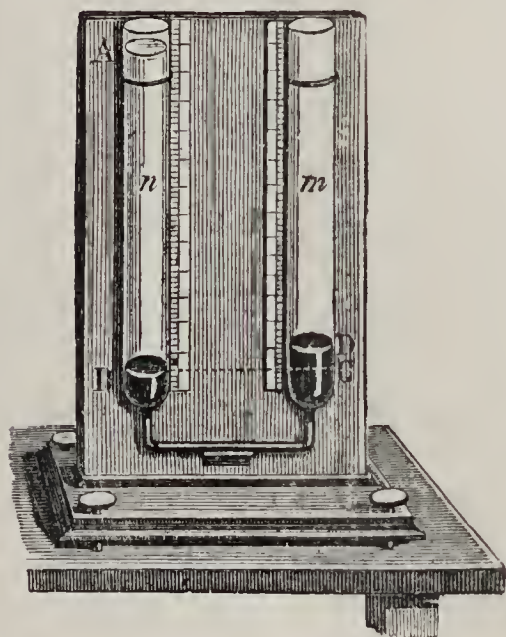


FIG. 26.

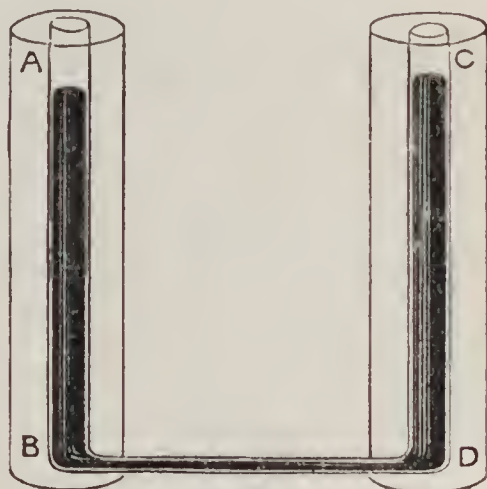


FIG. 27.

that is, the density of mercury is about $13\frac{1}{2}$ times the density of water. This ratio of their densities is independent of the diameter of the vessel.

It was by applying this principle that the first determinations of the absolute expansion of mercury were made by Dulong and Petit. Vertical tubes, A B, C D, were joined by a fine horizontal tube, B D (Fig. 27). Mercury was poured in, and of course stood at the same height in each tube. A B was surrounded with melting ice, and C D, we shall imagine, with a steam bath (it was really a bath of oil). Then, B D being in equilibrium, the pressure at D, due to the column D C and the pressure of the atmosphere equalled the pressure at B, due to the column A B and the pressure of the atmo-

sphere. The pressure of each column is due to the vertical height and the density of the liquid. If D_0 and D_{100} represent the density of mercury at 0° and 100° , and h and H the height of the mercury in each tube above B D, then—

$$D_0 h = D_{100} H \quad (\text{i.})$$

And if V_0 and V_{100} be the volumes of equal masses at the two temperatures (§ 27), then—

$$D_0 V_0 = D_{100} V_{100} \quad (\text{ii.})$$

$$\therefore \frac{V_{100}}{V_0} = \frac{H}{h}$$

$$\therefore \frac{V_{100}}{V_0} = \frac{V_0(1 + 100\Delta)}{V_0} = 1 + 100\Delta = \frac{H}{h}$$

Δ being the coefficient of the absolute expansion of mercury.

H and h were carefully measured, and thus $\Delta = \frac{H - h}{h \cdot 100}$ was determined.

The complete apparatus is shown in Fig. 28. A and B

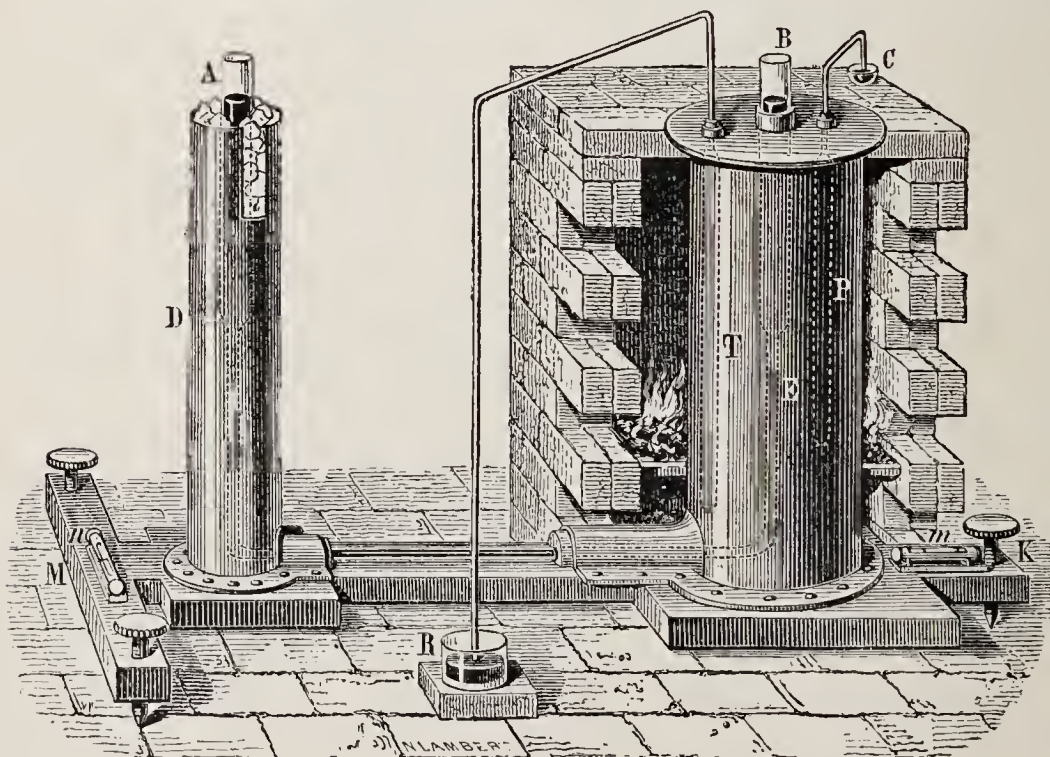


FIG. 28.

are the two tubes; E contains oil heated by the furnace; T R is an air-thermometer; and P C a weight thermometer for

determining the temperature of E. The vessel D is filled with melting ice; $m n$ are levels by means of which the stand M K is levelled.

The difficulty of keeping the mercury at a constant temperature and at a constant height, and of preventing the transference of heat from B to C, has led to the following modifications :—

32. Regnault's Method.—A B, C D are vertical tubes, continued above A and C, and open at the top (Fig. 29). They are joined by a horizontal tube, A C. B E, D F are horizontal tubes, into which vertical tubes, E K, F L, are inserted. These are joined together at the top by a tube, K L. Into K L opens a tube, $m n$, connected with a spherical vessel, P, of compressed air.

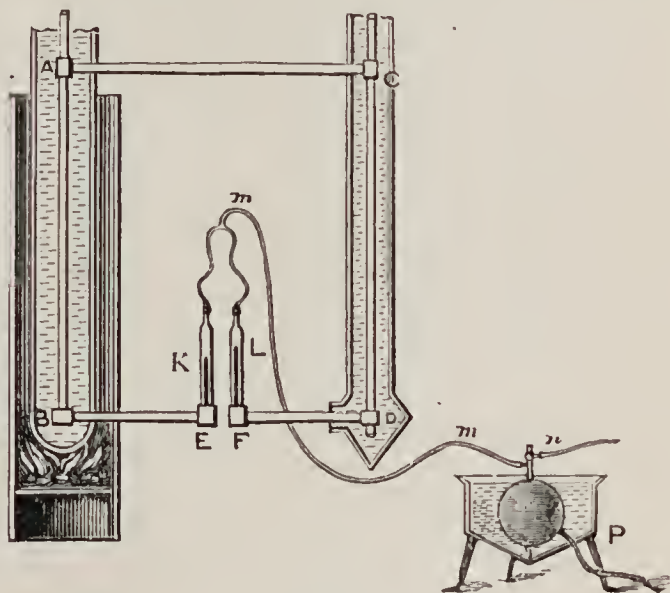


FIG. 29.

A B is surrounded with a bath of boiling oil; while into the bath C D water enters at the bottom and escapes at the top. The overflow water runs over K E, L F, and the parts of E B, F D not exposed to the baths, and keeps them at a constant temperature. Thermometers (not shown) are inserted in the baths, so that their temperatures can be accurately determined. Mercury is poured into A B, C D. The two parts are prevented from mixing by the air in K L. P is kept at a constant temperature by being surrounded by water, and more air can be forced in through n if necessary.

The air is compressed until the mercury is above the level A C. Seeing that A and C are in communication, the total pressure of mercury and atmosphere above A must equal that above C. The distances above A and C need not therefore be measured. The mercury fills A B E to K on the left side, and

C D F to L on the right side. Suppose all the temperatures steady, then the following observations are taken :—

H	=	the height of A above the tube B E.
h	=	„ „ K „ „ B E.
H_1	=	„ „ C „ „ D F.
h_1	=	„ „ L „ „ D F.

The pressure of the mercury at K is equal to the difference of the pressure due to the height of mercury H at T° and h at t° . Similarly, the pressure at L equals the difference due to the height H_1 at t° and the height h_1 at t° . These pressures are equal, being both equal to the pressure of the compressed air in M.

If Δ be the coefficient of absolute expansion, we have length H at $T^\circ = \frac{H}{1 + \Delta T}$ at 0° (see § 39). Reducing, similarly, all to 0° —

$$\frac{H}{1 + \Delta T} - \frac{h}{1 + \Delta t} = \frac{H_1}{1 + \Delta t} - \frac{h_1}{1 + \Delta t}$$

$$\therefore 1 + \Delta T = \frac{H}{H_1 + h - h_1} (1 + \Delta t)$$

If we assume that the coefficient of expansion can be expressed by a simple fraction, Δ is the only unknown quantity.

But Regnault made no such assumption. It was one of the objects of his research to discover whether the expansion of mercury was uniform or not. t would not be a high temperature, and therefore Δt would be small compared with ΔT .

He therefore assumed $\frac{1}{5550}$ or other suitable value from

Dulong and Petit's tables (p. 38), and calculated Δt ; substituting this value in the formula, he obtained an approximate value of ΔT as a whole, that is, the total dilatation. From this value of ΔT he determined the mean coefficient Δ , calculated Δt , and used this in the formula for determining the final value of ΔT . (See Worked Example 3, p. 56.)

33. Formulæ and Results.—This is a convenient place to note that the coefficients of expansion are not necessarily of the simple form we have assumed; that, for instance,

$V_t = V_0(1 + Kt)$ does not really represent the truth. If the coefficient of expansion were constant, and always equal to K , then the total dilatation for unit volume for any range of temperature, t , is Kt .

Suppose we mark off on $O X$ temperatures, and along $O Y$ volumes (Fig. 30). The position O on $O Y$ represents 10,000 volumes. Let us take the coefficient for mercury to be the mean between 0°C. and 100°C. , that is, 0.00018153 ; then a is the position for 100° , the distance from the temperature line to a being 181.5 ; for 200° it will be 363.1 , represented by b ; for 300° it will be 544.6 , represented by c . Joining the points $O a b c$, we form the straight dotted line.

Regnault's investigations showed that the relation was more accurately expressed by a curve, which was convex towards $O X$; that the actual volumes above 100°C. were greater than is indicated by the dotted line $O a b c$, while below 100° they were less. The continuous curve represents as carefully as is possible on this scale some of the results of Regnault's research.

The dilatation for t° (Δt), instead of being represented as Kt , is more accurately represented by three terms; thus—

$$\Delta t = at + bt^2 + ct^3$$

The constants have been determined that give accurate results between certain limits. The mean dilatation for one degree between these limits will be—

$$\frac{\Delta t}{t} = a + bt + ct^2$$

a and b and c are all three positive; and we see that the mean coefficient of expansion increases with the temperature.

A useful approximation for mercury is given by $\Delta t = at + bt^2$, where—

$$a = 0.0001801$$

$$b = 0.00000002$$

Thus unit volume at 0° would become at 50° —

$$\begin{aligned} V_{50} &= 1 + at + bt^2 = 1 + 0.0001801 \times 50 + 0.00000002 \times (50^2) \\ &= 1 + 0.009005 + 0.00005 = 1.009055 \end{aligned}$$

Regnault's experiments gave 1.009013 .

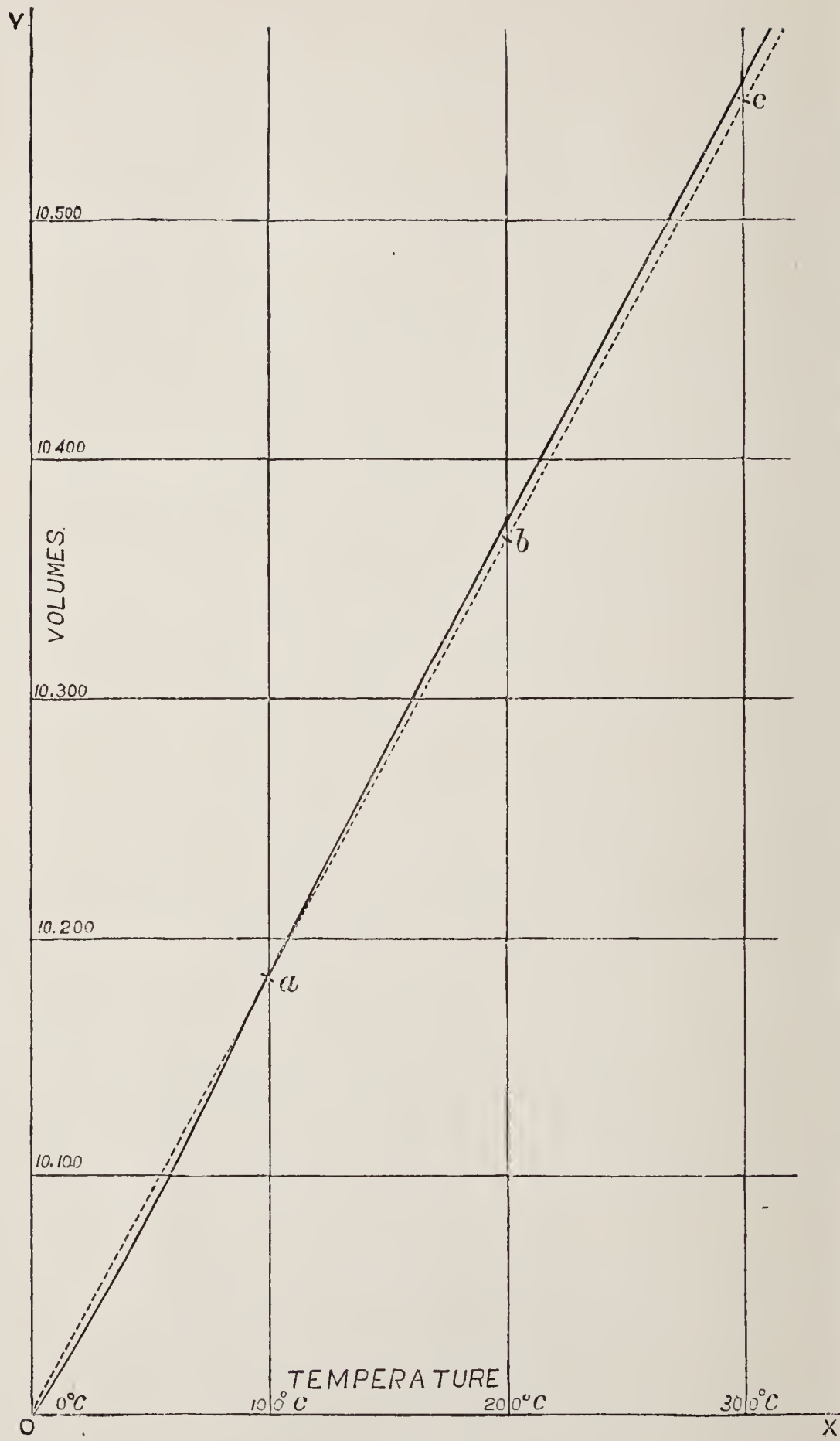
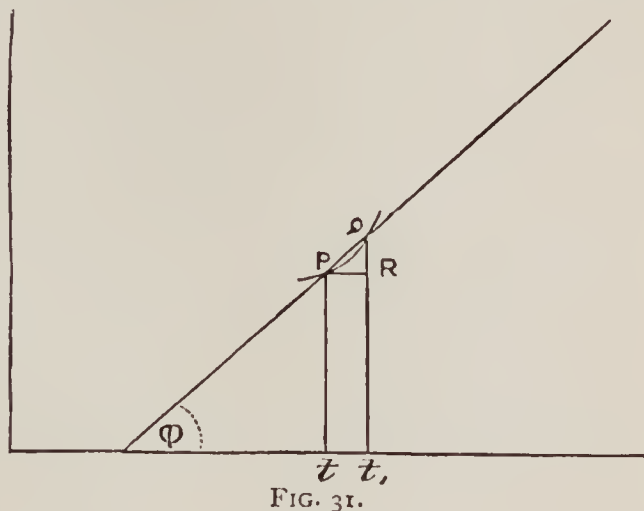


FIG. 39.

In finding the mean coefficient between two temperatures, we find the ratio between the increase in volume and the increase in temperature.

The true coefficient of expansion at any given temperature is found by taking a very small increase in volume, called dv , and dividing it by the small increase in temperature, say dt ; that is, we measure the rate of change of the volume as the temperature changes, so that the coefficient $c = \frac{dv}{dt}$. In

Fig. 31, when temperature increases from t to t_1 , the volume increases



by QR . Then the coefficient is $\frac{QR}{t_1 - t} = \frac{QR}{PR} = \tan \phi$. If t_1 be very near t , so that Q moves to P , $\frac{QR}{PR}$ becomes the tangent of the curve at the point P , and measures the *true coefficient* of expansion at t° .

The form of the curve (Fig. 30) shows that the true coefficient will increase as the temperature is raised.

TABLE OF THE DILATATIONS OF MERCURY.

Temperature t° .	Volume at each temperature t° .	Mean coefficient of expansion from 0° to t° .	<i>True coefficient</i> of expansion at t° .
0° ...	1.000000	... 0.00000000	... 0.00017905
20° ...	1.003590	... 0.00017951	... 0.00018001
40° ...	1.007210	... 0.00018002	... 0.00018102
60° ...	1.010831	... 0.00018052	... 0.00018203
80° ...	1.014482	... 0.00018102	... 0.00018304
100° ...	1.018153	... 0.00018153	... 0.00018405
200° ...	1.036811	... 0.00018405	... 0.00018909
300° ...	1.055973	... 0.00018658	... 0.00019414

The increase in the true coefficient of expansion, and the

difference between the true and mean coefficients, are very small, and probably the student will not be called upon in any ordinary experiments or calculations to use such exact figures. The table is given to illustrate the present section, and to accentuate the fact that, while for ordinary purposes it may be sufficient to use a simple form for the coefficient of expansion of mercury (or other substance), the physical facts may not be as simple as the form would suggest, and that it is only by laborious experiments that the actual truth can be reached. Later researches have slightly altered the figures given, and probably as the skill of experimenters increases and apparatus is improved, further slight alterations will be needed. These remarks will be further illustrated throughout the book, notably when we treat of what to the beginner are the simple laws of Boyle and Charles. Analogous results are obtained for other liquids. The case of water will be treated in § 35.

34. Maximum Density of Water.—

The experiments of Hope showed that, if water be gradually cooled down to the freezing point, its volume does not decrease continuously; that is, that its maximum density is not, as we might expect, at 0° C.

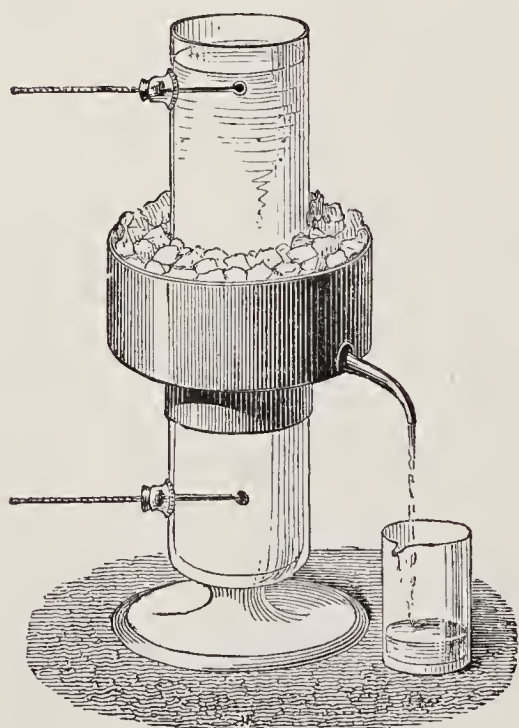


FIG. 32.

A tall jar is fitted with two thermometers in a horizontal position (Fig. 32). The jar is filled with water at 0° , and is then brought into a room at, say, 10° . The water at the side becomes heated, and rises, the lower thermometer indicating a lower temperature than the upper until the

lower registers 4° C. The upper falls to 4° , and gradually to 0° , while the lower remains at 4° . Evidently the density of water at 4° is greater than it is at 0° .

The converse experiment is made by filling the jar with water at 6° or 7° , and then taking it into a room at 0° . At first the lower thermometer indicates a lower temperature until the whole sinks to 4° . The lower then remains at 4° , while the upper falls to freezing point.

The jacket of ice (Fig. 32) is placed round for the purpose of a lecture experiment. The cooled water sinks until 4° is reached, then the water at 4° remains at the bottom, and the water at 3° , 2° , 1° , 0° rises, and the upper thermometer falls to freezing point.

In nature the result is that the surface water of ponds and lakes sinks until the temperature of the whole is at 4° . The next layer, cooled below 4° C., floats until its temperature sinks to 0° . It then freezes, and the density of ice being less than water, the ice floats, and thus the general temperature of the latter is prevented falling below 4° , and fishes and plants that would otherwise perish are preserved.

35. Absolute Expansion of Water.—We have seen (§ 29) that the weight thermometer can be used for determining the expansion of water (or other liquid). Knowing the absolute expansion of mercury, we can measure the apparent expansion when enclosed in a particular kind of glass, and deduce the expansion of the glass. Filling the thermometer with water, we can determine the apparent expansion of water, and then deduce the absolute expansion of water (§ 30). In practice this method is found to be defective. The density of water is only about $\frac{1}{14}$ that of mercury, and the amounts expelled are therefore small; errors are also introduced by evaporation.

Thermometer Method.—A better plan is to use a large graduated thermometer. The coefficient of expansion of the kind of glass is determined by making part into a weight thermometer. The tube is calibrated carefully (§ 6), and the volume of the bulb is determined by filling the bulb and a certain number of divisions with mercury, weighing, and deducting the weight of the glass. This gives a mass, M , of mercury; then, if D be the density of mercury at the given temperature, we have $V_t = \frac{M}{D}$; that is, the volume is known at t° . Also $V_0 =$

$\frac{V_t}{1 + ct}$, where c is the dilatation of glass from 0 to t degrees.

We next determine the volume of a division of the stem by introducing a thread of mercury, observing its length and the number of divisions it covers. If m be the weight of the thread, and n the number of divisions, and t the temperature—

$$\begin{aligned}\frac{m}{D} &= v_t; \text{ also } v_0 = \frac{v_t}{1 + ct} \\ \therefore \frac{v_0}{n} &= \frac{v_t}{n(1 + ct)} = \frac{m}{nD(1 + ct)}\end{aligned}$$

= volume of each division at 0° , and the volume at any other temperature is easily calculated. (D = density at t° .)

The whole of the mercury is expelled, and the liquid introduced; its volume (v_t) at t° is observed. It is then heated to various temperatures, the new volume noticed, and thus the apparent expansion between 0° and a series of temperatures t_1, t_2 , etc., is determined. The absolute expansion is then obtained, knowing the expansion of the glass. The expansion of water has been carefully studied by this method.

If the water be thoroughly freed from air, it has the property of remaining liquid at temperatures down to -20°C. , so that the dilatation can be examined down to this temperature. The maximum density of water is found to be at 4°C.

The Areometric Method.—This method was first used by Matthiesson to determine the absolute expansion of water. A delicate balance is required. A long fine platinum wire passes from the end of one arm through a hole in the bottom of the case, and dips into a bath of pure water, which can be kept at a constant temperature. The steps are as follows:—

(1) A piece of glass rod, whose linear expansion has been determined accurately by the ordinary method, is weighed in air. Let its mass be m .

(2) The solid is attached to the platinum wire, and weighed when immersed in pure water at two definite temperatures. Let us take the temperatures at 0° and 100° ; and let the weights be m_0 and m_{100} .

Then $\mu_0 = m - m_0 =$ weight of water displaced at 0°C .
 And $\mu_{100} = m - m_{100} =$ " " " " 100°C .

(3) Let c be the linear coefficient of expansion of glass.

Then $3c = K =$ coefficient of cubical expansion.

Let α be the mean coefficient of expansion of water between the two temperatures.

$\frac{m}{\mu_0} =$ spec. gravity of the solid when solid and water are at 0°
 $\frac{m}{\mu_{100}} =$ " " " " 100°

If D and d represent the density of glass and water, then $\frac{D_0}{d_0}$ and $\frac{D_{100}}{d_{100}}$ also equal the specific gravity of the solid under the two conditions.

$$\therefore \frac{m}{\mu_0} = \frac{D_0}{d_0}, \text{ and } \frac{m}{\mu_{100}} = \frac{D_{100}}{d_{100}}$$

$$\text{Also } D_{100} = \frac{D_0}{1 + 100K} \text{ and } d_{100} = \frac{d_0}{1 + 100\alpha}$$

$$\begin{aligned} \therefore \frac{m}{\mu_{100}} &= \frac{D_{100}}{d_{100}} = \frac{\frac{D_0}{1 + 100K}}{\frac{d_0}{1 + 100\alpha}} = \frac{D_0}{d_0} \cdot \frac{1 + 100\alpha}{1 + 100K} \\ &= \frac{m}{\mu_0} \cdot \frac{1 + 100\alpha}{1 + 100K} \end{aligned}$$

$$\therefore 100\alpha = \frac{\mu_0}{\mu_{100}} (1 + 100K) - 1$$

All the quantities are known save 100α .

If the two temperatures be t_1 and t_2 , the student will be able to show that—

$$\frac{1 + t_1\alpha}{1 + t_2\alpha} = \frac{\mu_1}{\mu_2} \cdot \frac{1 + t_1K}{1 + t_2K}$$

(See Worked Examples, No. 4, p. 56.)

36. Direct Measurement of Cubical Expansion of Solids.—The cubical dilatation of solids has been determined in § 25, from the linear dilatation. If we know the absolute

expansion of any liquid, we can determine the cubical expansion of a solid direct by weighing it in air and in the liquid.

If, for example, by any other method (Regnault's) we know accurately the expansion of water, then we can use the areometer to determine the cubical expansion of solids; that is, in the last formula all the quantities are known save K .

TABLE.

The following represent some mean values of the volume occupied by water, whose volume is unity at 4° C. :—

-2° . 1'000308	7° . 1'000066
0° . 1'000130	8° . 1'000166
1° . 1'000072	10° . 1'000260
2° . 1'000032	15° . 1'000855
3° . 1'000008	20° . 1'001746
4° . 1'000000	40° . 1'007695
5° . 1'000008	60° . 1'016919
6° . 1'000030	100° . 1'043130

By either of the methods in § 35 it is found that a given mass of water occupies a minimum volume at a temperature that is practically 4° C. Dividing the volume at any temperature by the volume at 4° , we obtain the volume that unit volume occupies at various temperatures. An examination of the table shows that the rate at which the volume increases from 4° C. increases with the temperature; that is, the mean coefficient of expansion of water, and also the true coefficient at any temperature, increase, with the temperature.

Following the plan in § 33 for mercury, empirical formulæ have been devised for water and other liquids. Generally the form is—

$$V_t = V_0(1 + at + bt^2 + ct^3)$$

where a , b , and c have to be determined for each liquid.

Mendeléeff has shown that if the density of water at 4° C. under a pressure of 1 atmosphere be unity, then the density at any other temperature—

$$D_t = 1 - \frac{(t - 4)^2}{1000\phi(t)}$$

where $\phi(t) = 125.78 + 1.158t - 0.0019t^2$.

This gives the density at 10° C. = $1 - \frac{36}{1000(137.17)}$
 = $1 - 0.000262 = 0.999738$.

\therefore unit volume at 4° C. = $1 \div 0.999738 = 1.000262$

The density at 100° C. by the same formulæ becomes 0.958595 and volume 1.043194.

The formula gives good results between -10° C. and 100° C.

37. Other Liquids.—The coefficients of expansion generally increase with the temperature, and liquids near the boiling point show a marked increase.

This is shown in the following table.¹ The temperature after the liquid is that of its boiling point:—

VOLUMES.

Temperature.	Alcohol. 78°.	Ether. 35°.	Bisulphide of carbon. 46°.	Water. 100°.	Air.
0°	1.0	1.0	1.0	1.0	1.0
10°	1.01050	1.01518	1.01156	1.00013	1.0367
20°	1.02128	1.03122	1.02350	1.00161	1.0734
30°	1.03242	1.04829	1.03594	1.00414	1.1101
40°	1.04404	1.06654*	1.04901	1.00756	1.1348

* Under increased pressure.

Air is added for reference.

By subjecting the liquids to pressure, they can be kept in the liquid form at temperatures above their ordinary boiling points, which are determined under normal atmospheric pressure. The coefficients are then found to increase rapidly. Thus liquid carbonic acid between 0° and 30° has a coefficient four times greater than that of air. Water at 180° C. has a coefficient nearly half that of air, while the coefficient of alcohol at 160° C. is nearly five times that of air.

38. Graham's Pendulum.—In its simplest form it consists of a steel (or other metal) rod attached to a cylindrical glass vessel containing mercury for a bob. With a rise of

¹ Everett's "Physical Constants."

temperature, the steel expands, and lengthens the pendulum; the mercury also expands, and thus raises the centre of gravity of its mass.

Between 0° and 40° —

The linear coefficient of expansion of steel is 0.000012

The cubical „ „ mercury „ 0.000180

If, therefore, the rod be attached to the base of the cylinder the pendulum will compensate, neglecting small corrections when the length of the steel rod is to the length of the column of mercury as $180 : 12 = 15 : 1$.

39. Barometric Corrections.—The pressure of the atmosphere is measured by the pressure of a column of mercury of an observed height on a given area; the normal pressure is equal to that of a column of mercury 760 mm. high per unit of area, say per square millimetre. To determine the pressure we determine the weight of 760 cubic mm. of mercury: this equals $760 \times$ weight of 1 cubic mm.

As the density of mercury changes with the temperature, it is necessary to have some standard temperature; this temperature on the Centigrade scale is 0° C. If, therefore, the height 760 mm. be observed at 15° , the true height will be the height this column would assume if the temperature were 0° .

(1) Barometric readings will not usually be taken at a higher temperature than 40° C., therefore we may take the coefficient of mercury as 0.00018 .

If L be the length of the column, then—

$$L_t = L_0(1 + 0.00018t)$$

$$\therefore L_0 = L_t \frac{1}{1 + 0.00018t} = L_t(1 - 0.00018t) \quad (\S 27.)$$

L_0 is called the true reading of the barometer.

$$L_0 = L_t - 0.00018t \cdot L_t$$

Seeing that 0.00018 is small, and the barometer will not vary in these latitudes much from 760 mm., we may write—

$$\begin{aligned} L_0 &= L_t - 0.00018 \times 760 \times t \\ &= L_t - 0.137t \end{aligned}$$

that is, from the observed reading in millimetres subtract $0.137 \times \text{temperature}$.

Thus if the barometer reading be 763.6 at 15° , the true reading

$$\begin{aligned} &= 763.6 - 0.137 \times 15 \\ &= 763.6 - 2.055 \\ &= 761.545 \text{ approximately} \end{aligned}$$

The true value would be $763.6 - 2.061 = 761.539$.

(2) Not only has the column of mercury expanded, but the scale (generally brass) on which the graduations are marked has also expanded, and therefore the true reading will be *greater* than the observed reading. The scale is generally made correct at 0°C . Since the expansion of mercury is to the linear expansion of brass as $18 : 19$, this correction will be less than that due to the expansion of mercury.

If l be the observed length of the scale, the true length will be—

$$l(1 + 0.000019t) = l + 0.000019lt$$

Again, taking a mean value for $l = 760$

$$= l + 0.01444t$$

In the above example the correction for the brass scale will be—

$$0.01444 \times 15 = 0.217$$

\therefore making both corrections, the true reading is—

$$763.6 - 2.05 + 0.22 = 761.77 \text{ mm.}$$

Generally, if a barometer scale be correct at 0° , any observed reading l in mm. at t° needs two corrections: (a) mercury, $-Klt$; (b) scale, $+\beta l$.

$$\therefore \text{true reading} = l - l(K - \beta)t$$

For brass and mercury this becomes—

$$\begin{aligned} &l - l(0.00018 - 0.000019)t \\ &= l - l(0.000161)t \end{aligned}$$

or, taking a mean value of $l = 760$

$$= l - 0.122t$$

Sometimes the graduations are on the glass itself. In this case the true reading

$$\begin{aligned}
 &= l - l(0.00018 - 0.0000085) \\
 &= l - l(0.0001715) \\
 &= l - 760(0.0001715) \\
 &= l - 0.129t
 \end{aligned}$$

Other corrections are (a) those due to capillarity. This requires a small quantity, depending upon the diameter of the tube, to be added to the result. If the tube be 5 mm. in diameter, then 1.54 mm. must be added to the observed height; if 3 mm., then 1.22 mm. The exact figures can be taken from proper tables.

(b) The student will see, after § 97, that the pressure of mercury vapour is appreciable, and will depress the column, and thus a further amount must be added.

Having made the four corrections: (1) mercury, (2) scale, (3) capillarity, (4) vapour pressure, we obtain the true height of the barometer. This equals the pressure of the atmosphere near the barometer when the reading is taken.

40. Pressure of the Atmosphere.—If, after all the above corrections have been made, the true height is 750 mm., then the pressure of the atmosphere is equivalent to the pressure of 75 cubic cm. per square centimetre.

The density of mercury at $0^\circ = 13.596$.

\therefore the pressure of the atmosphere per square centimetre equals the weight of a volume of mercury whose mass is 75×13.596 grams = 1019.7 grams per square centimetre

This will depend upon g , the acceleration due to gravity. For purposes of comparison the standard value of the acceleration due to gravity (g_0) is taken at the sea-level in latitude 45° N. If, after the above corrections, the height of the barometer is h_1 in the latitude ϕ , and at a height h in metres above the sea-level, and g_1 be the acceleration due to gravity under these conditions, it can be shown that—

$$\frac{g_1}{g_0} = 1 - 0.0026 \cos 2\phi - 0.0000002h$$

then if l_0 be the reading for $g = g_0$ —

$$l_0 g_0 = l_1 g_1$$

$$\therefore l_0 = l_1 \frac{g_1}{g_0} = l_1 (1 - 0.0026 \cos \phi - 0.0000002h)$$

The last part of the expression can generally be neglected unless it be greater than 1000 metres, *i.e.* than 3281 feet.

WORKED EXAMPLES.

1. A weight thermometer when empty weighs 11.5 grams; filled with mercury at 13°C. , it weighs 141.56 grams. After heating to 100° the weight is 139.86 grams. The cubical expansion of glass has been found to be 0.0000264. Find (1) the apparent expansion of mercury in glass; (2) the absolute expansion of mercury in glass.

The vessel contains 130.06 grams at 13° and 128.36 grams at 100° .

\therefore 1.7 gram has been expelled

The apparent expansion can be calculated from the formula in § 28, or the result can be obtained thus—

Since we are not concerned with the expansion of glass, we may regard the glass as being inexpandible. The thermometer is full at 100° and at 13° ; that is, 130.06 grams at 13° and 128.36 grams at 100° each occupy the same volume, V .

$$\text{The volume of unit mass at } 13^\circ = \frac{V}{130.06}$$

$$\text{,, ,, ,, } 100^\circ = \frac{V}{128.36}$$

$$\therefore \text{dilatation of unit mass} = V \left(\frac{1}{128.36} - \frac{1}{130.06} \right)$$

\therefore mean coefficient of apparent expansion of mercury between 13° and 100°

$$\begin{aligned} &= \frac{\text{increase in unit volume}}{\text{unit volume} \times 87} = \frac{V \left(\frac{130.06 - 128.36}{128.36 \times 130.06} \right)}{V \cdot \frac{1}{130.06} \times 87} = \frac{1.7}{128.36 \times 87} \\ &= 0.000152 \end{aligned}$$

\therefore coefficient of absolute expansion = coefficient of apparent expansion + expansion of glass = $0.000152 + 0.0000264 = 0.000178$

2. The coefficient of absolute (cubic) expansion of mercury is 0.00018; the coefficient of linear expansion of glass is 0.000008. Mercury is placed in a graduated tube, and occupies 100 divisions of the tube. Through how many degrees of the tube must the temperature be raised to cause the mercury to occupy 101 divisions? (London Matric., 1883.)

If t be the number of degrees, then the length of the mercury column becomes $100(1 + 0.00018t)$.

These equal 101 divisions of the glass after expansion.

$$\therefore 1 \text{ glass division} = \frac{100(1 + 0.00018t)}{101}$$

1 glass division becomes $(1 + 0.000008t)$ divisions at t°

$$\therefore 100(1 + 0.00018t) = 101(1 + 0.000008t)$$

$$\begin{aligned}\therefore t &= \frac{1}{0.018 - 0.000808} = \frac{1}{0.017192} \\ &= 58.2^\circ \text{ C.}\end{aligned}$$

3. In an experiment for determining the absolute expansion of mercury by Regnault's method, the temperature (T) of the bulb A B is 100° , that of C D and the tubes E K, F L, is the temperature (t) of the room, 10° C. ; the height of B A (H) is 1010 mm., D C (H_1) is 1009 mm., E K (h) is 101.2 mm., and F L (h_1) is 117.4 mm.: find the dilatation of mercury between 0° and 99° C.

$$1 + \Delta T = \frac{H}{H_1 + h - h_1} (1 + \Delta t) = \frac{1010}{1009 + 101.2 - 117.4} \left(1 + \frac{10}{5550}\right)$$

(assuming $\frac{1}{5550}$ as the mean dilatation from Dulong and Petit's tables).

$$\therefore 1 + \Delta T = \frac{1010}{993.8} \cdot \frac{5560}{5550} = 1.018132$$

$$\therefore \text{dilatation from } 0^\circ \text{ to } 100^\circ \text{ C.} = \Delta T = 0.018132$$

We can now state that $0.018132 \div 100$ is more accurate than $\frac{1}{5550}$ for the mean dilatation; we can therefore substitute this mean value.

$$\therefore 1 + \Delta T = \frac{1010}{993.8} (1.0018132) = 1.018154$$

$$\therefore \Delta T = 0.018154$$

Similarly, ΔT as a whole was determined at the various temperatures.

4. A cylindrical piece of glass ($k=0.0000085$) weighs 4.525 grams in air, 2.817 grams when immersed in water at 20° C. , and 2.881 grams in water at 100° C. : find the dilatation of water between 20° and 100° C. (See § 35.)

$$\begin{aligned}\mu_{20} &= 4.525 - 2.817 = 1.708 \text{ gram}; \quad \mu_{100} = 4.525 - 2.881 = 1.644 \text{ gram}; \\ K &= 0.0000255\end{aligned}$$

$$\therefore 80K = 0.00204$$

$$(80a) = \frac{1.708}{1.644} (1 + 0.00204) - 1 = 0.041$$

$$\therefore \text{unit volume at } 20^\circ \text{ C.} = 1.041 \text{ at } 80^\circ \text{ C.}$$

(For further examples on chapter III., see p. 77.)

CHAPTER IV.

DILATATION OF GASES.

41. Boyle's Law.—The dilatation of gases is complicated by the fact that not only temperature but pressure must be considered. The compressibility of solids and liquids is so small that it does not affect appreciably any of the results. With gases it is otherwise.

The relation between the volume and pressure of a gas was first formulated by Boyle.

The experiments can be repeated by taking a bent tube about 50 inches long, closed at the end of the short limb, which should be about 7 inches. On pouring a little mercury down it can be arranged so that it stands at the same level in both limbs. We have then a certain volume of air cut off from the rest of the atmosphere, and subject to the pressure of the atmosphere; this we read from the barometer. Measure the length of the column of air in the short limb, and read the thermometer. Pour mercury into the long limb. The air in the short limb is compressed. When it cools to the temperature of the room, measure also (*a*) the height of the mercury in the long limb above the level of the mercury in the short limb; this, with (*b*) the pressure of the atmosphere, gives the total pressure to which the air is subjected. Make several such measure-

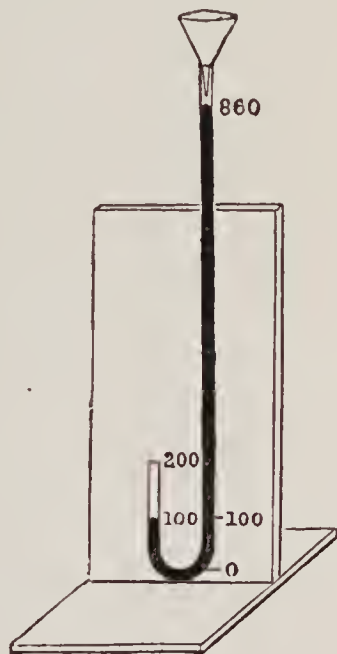


FIG. 33.

ments, and record as follows. The measurements are made in millimetres :—

	V Volume.	(a) Pressure of mercury.	(b) Pressure of atmosphere (barometer).	P Total pressure (a + b).	V × P.
1	221	143	756	899	198,679
2	176	378	„	1134	199,584
3	112	1023	„	1779	199,248
4	102	1200	„	1956	199,512
5	95	1346	„	2102	199,690
Average 					199,522

Allowing for errors of measurements, we see that the general law of Boyle can be accepted—

If a given mass of gas be kept at the same temperature, the product of the volume and pressure is a constant ; or, the volume varies inversely as the pressure.

$$P \times V = \text{constant}$$

Clasping the short limb with the warm hand produces expansion, and shows at once the reason for the insertion of the words, “at a given temperature.”

42. Isothermals.—These results may be represented graphically by taking O X, O Y as the co-ordinates, measuring along O X distances proportional to the volume, and along O Y distances proportional to the pressure. This is readily done by using squared paper. In Fig. 34 each side of a square represented a volume of 5 mm. (the paper was divided into $\frac{1}{10}$ inch; only the inch-lines are shown), and, measuring vertically, each side represented a pressure equal to 50 mm. of mercury. Thus to represent the first line of the table, O a was

made equal to $\frac{221}{5} = 44.2$ sides of squares; a A was made

equal to $\frac{899}{50} = 19$ sides of squares. Similarly, the points

B, C, D, E were obtained for lines 2, 3, 4, and 5 of the table. F, G, H were similarly calculated. The points A, B, . . . G, H are joined by a free curve that passes through or near

them all; any point off this curve probably denotes some experimental error.

If the gas obeys exactly Boyle's law, the isothermal is a

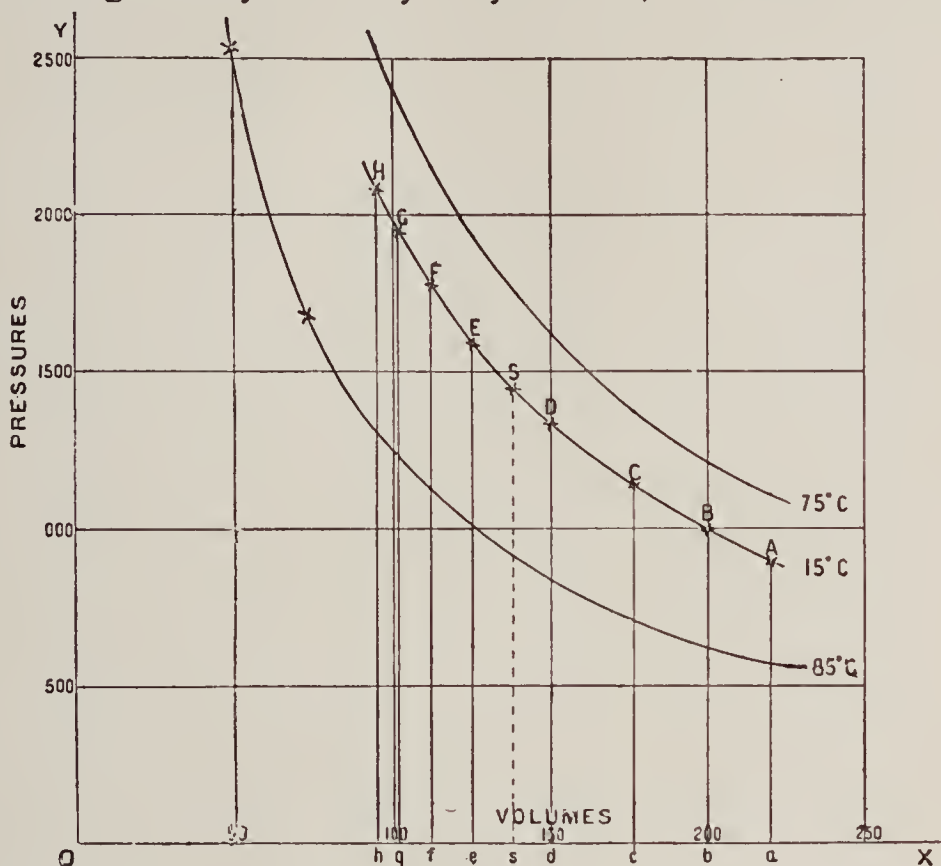


FIG. 34.

rectangular hyperbola. Practically the curves in Fig. 34 are such curves.

This curve, representing the relation between the volume and pressure of a gas when the temperature remains constant, is called the isothermal of a given mass of the substance for that temperature.

The particular curve A . . . H is an isothermal for air at 15°C.

By surrounding the short limb of the Boyle tube with a vessel containing water at 75°, we could similarly plot the results, and obtain the isothermal for the same mass of air at 75°. It would lie above the curve drawn, as that for -85° would lie below the curve.

If we take any point, S, and draw S s, then the meaning of the point S is that the pressure of the gas is measured by S s, and the volume by O s; in figures the pressure is 1456 and the volume 137: ($1456 \times 137 = 199,472$).

If P_1 represent a pressure of 1 atmosphere, and V_1 the volume at that pressure, similar meanings being attached to P_2 (2 atmospheres), V_2 , etc., then for gases that obey Boyle's law—

$$P_1V_1 = P_2V_2 = P_3V_3 = \text{etc.} = \text{a constant}$$

$$\therefore \frac{P_1V_1}{P_2V_2} = \frac{P_2V_2}{P_3V_3} = \text{etc.} = 1$$

When the pressure is between 1 and 2 atmospheres, it is found that at ordinary temperatures gases such as air, hydrogen, nitrogen, oxygen, which we shall find are gases that are liquefied with difficulty, practically fulfil the conditions $\frac{P_1V_1}{P_2V_2} = 1$

In the case of gases like carbonic acid and sulphur dioxide, which we shall find are gases that are easily liquefied at ordinary temperatures, the ratio $\frac{P_1V_1}{P_2V_2}$ is greater than unity. If, therefore, we draw the isothermal for 15° for sulphur dioxide, beginning at a pressure of 1 atmosphere, when we reach a pressure of 2 atmospheres the volume will be less than that given by Boyle's law; the isothermal will fall slightly below the isothermal of a perfect gas.

The higher the temperature, however, the less the difference becomes. This is readily seen from the following values of the ratio $\frac{P_1V_1}{P_2V_2}$ for the two gases at various temperatures:—

Sulphur dioxide.			Carbon dioxide.		
$15^\circ \dots$	\dots	1.0185	$5^\circ \dots$	\dots	1.0065
$50^\circ \dots$	\dots	1.0110	$50^\circ \dots$	\dots	1.0036
$100^\circ \dots$	\dots	1.0054	$100^\circ \dots$	\dots	1.0023
$150^\circ \dots$	\dots	1.0032	$150^\circ \dots$	\dots	1.0014
$200^\circ \dots$	\dots	1.0021	$200^\circ \dots$	\dots	1.0008
$250^\circ \dots$	\dots	1.0016	$250^\circ \dots$	\dots	1.0006

It seems probable that at yet higher temperatures the ratio will approximate to unity.

We can, then, use Boyle's law at ordinary pressures for

gases that are not readily liquefied, and for liquefiable gases for temperatures far above their boiling points.

43. Boyle's Law at High Pressures.—Research has also been directed to discover whether gases conform to Boyle's law at high pressures.

Fig. 35 embodies Cailletet's experiments on nitrogen at 15°C . He found that the value of PV , beginning at a pres-

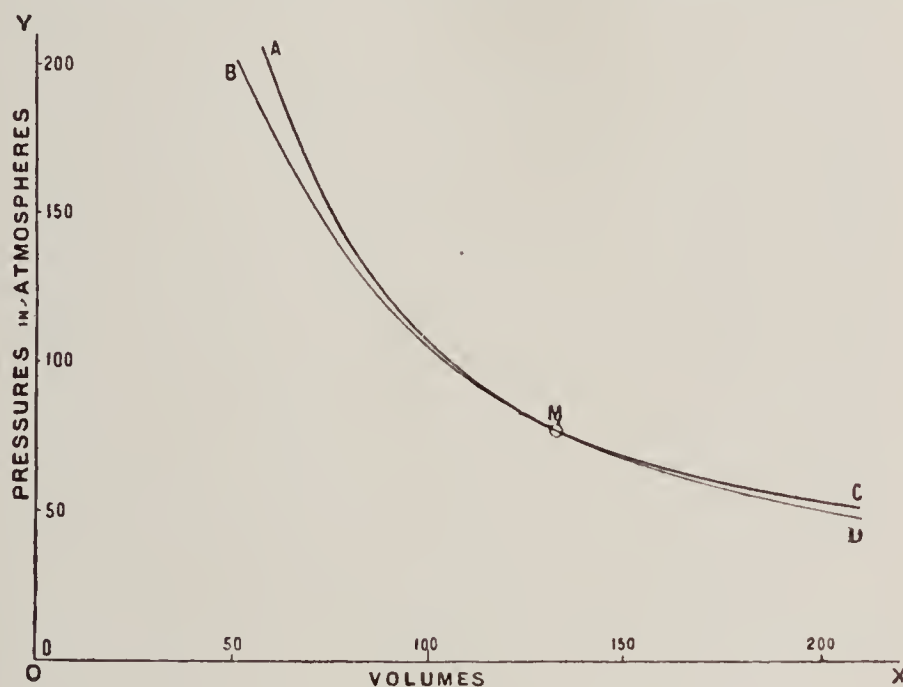


FIG. 35.

sure of 52 atmospheres, was 8184. It then gradually decreased, until, at a pressure of 78 atmospheres, it was 7900; it then gradually increased, and at a pressure of 252 atmospheres it was 9330. The minimum value is indicated at M. A M C is the isothermal for nitrogen at 15° , B M D the isothermal of a perfect gas passing through M. The isothermals for oxygen and air are similar to nitrogen, and lie above the isothermal of the perfect gas; the minimum value of PV for air is at a pressure of about 83 atmospheres; that of oxygen about 132 atmospheres.

In the case of hydrogen there is a *maximum pressure*; its isothermal at high pressure would meet the isothermal of a perfect gas at one point, and would otherwise be entirely below it (see also § 48).

44. Gay Lussac's Law.—Gay Lussac examined the

dilatation of gases when the pressure was kept constant and the temperature varied. He took a thermometer bulb and tube carefully calibrated, and estimated, as in § 6, the volume of the tube and each division of the stem. Filling it with dry mercury, he inverted it over a tube of calcium chloride, and, by moving a platinum wire, made the mercury fall out (Fig. 36). Its place was taken by air dried by passing over the calcium chloride. A slight thread of mercury was left in. This cut off the imprisoned air from the atmosphere, and served as an index.



FIG. 36.

The tube A B (Fig. 37) was now placed in a horizontal position; among melting ice, and the position of the index noted, the calcium chloride tube C still being kept in position. Thus the volume was known of a mass of air at 0° and at the pressure of the atmosphere. It was now placed in a similar position in a bath of water or oil (Fig. 37), which was gradually heated, the position at various temperatures being observed from the thermometers E and D. Neglecting the slight increase due to the expansion of glass, and assuming that the barometer remained steady, Gay Lussac was thus able to calculate the coefficient of expansion of air and other

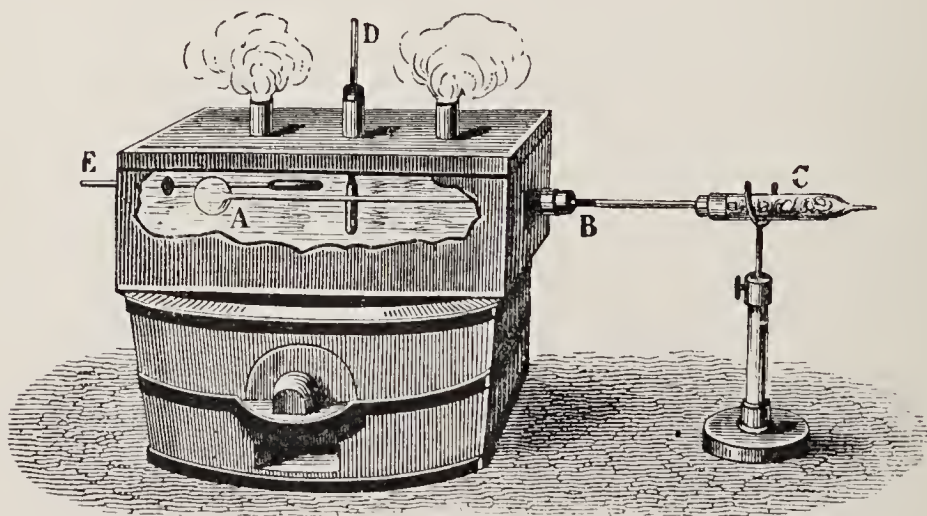


FIG. 37

gases. It was simply necessary to take the volume at zero from

the volume at t° , and divide by the volume at zero; this gave the dilatation for t° , and, dividing this by t , he obtained the mean for 1° . He concluded—

(1) All dry gases have the same coefficient of expansion if the pressure remains constant; and that the coefficient is the same at all pressures.

(2) The volume increases by a definite fraction of its volume for each rise in its temperature.

The first part of the law was discovered by Charles, and is sometimes known by his name.

Gay Lussac determined the coefficient of expansion for 1° to be 0.00365 ; this nearly equals $\frac{1}{273}$. Thus unit volume at 0° becomes $1 + \frac{1}{273}$ at 1° , $1 + \frac{2}{273}$ at 2° , and $1 + \frac{t}{273}$ at t° , and $1 + \frac{T}{273}$ at T° . Therefore—

$$\frac{\text{volume at } t}{\text{volume at } T} = \frac{1 + \frac{t}{273}}{1 + \frac{T}{273}} = \frac{273 + t}{273 + T}$$

If we write the coefficient as α , then

$$V_t = V_0 (1 + \alpha t)$$

$$\frac{V_t}{V_T} = \frac{V_0(1 + \alpha t)}{V_0(1 + \alpha T)} = \frac{1 + \alpha t}{1 + \alpha T} = \frac{273 + t}{273 + T}$$

45. Absolute Zero.—The law holds good for some distance below zero. Let us assume that it holds good for all temperatures below zero; then 273 units of volume at 0° become $273 - 1$, $273 - 10$, etc., at -1° , -10° , etc. At -273° evidently the volume would be *nil*. Now, we have no knowledge of such a low temperature, when all the heat will have left the gas, and cannot conceive of a gas existing without volume. But calling this temperature the *absolute zero*, and measuring temperatures from it, this and other laws are simplified in expression. 0° C. becomes 273° ; 15° C., $273 + 15^\circ$; and -10° , 263° .

We get from § 44—

$$\frac{V_t}{V_T} = \frac{273 + t}{273 + T}$$

i.e., if the pressure remains constant, the volume of a gas is proportional to the temperature measured from absolute zero.

The coefficient of expansion, using the Fahrenheit scale, is nearly $\frac{1}{493}$; therefore the absolute zero will be $493 - 32 = 461$ degrees below zero on that scale, that is, -461°F .

46. Relation between Volume, Pressure, and Temperature of Gases.—Suppose a given mass of a gas to be represented in volume, pressure, and temperature by V_t , P_t , and t . Now let it change in any way, the new values being $V_{t'}$, $P_{t'}$, and t_1 .

V_t at t° and P_t pressure will be $\frac{V_t}{1 + at}$ at 0° and P_t pressure.

$V_{t'}$ at t_1° and $P_{t'}$ will be $\frac{V_{t'}}{1 + at_1}$ at 0° and $P_{t'}$ pressure. Both are at the same temperature, 0°C .

Therefore by Boyle's law, $\frac{V_t}{1 + at} \cdot P_t = \frac{V_{t'}}{1 + at_1} \cdot P_{t'} =$ for any other temperature t_2° , and pressure $P_{t''}$, $\frac{V_{t''}}{1 + at_2} \cdot P_{t''}$; thus $\frac{V_t P_t}{1 + at}$ for any given mass of gas is a constant.

This combines the two laws. If we measure from absolute zero, we have $\frac{V_t P_t}{273 + t} = \text{constant} \times 273 = \text{constant}$, and $\frac{VP}{T}$ becomes a constant, if T represents the temperature measured from absolute zero.

\therefore relation between pressure and temperature of gases is—

$$\frac{V_0 P_0}{1 + a \cdot 0} = \frac{V_t P_t}{1 + at} = \frac{VP}{T} = \text{constant}$$

If the volume does not vary, we have—

$$P_0 = \frac{P_t}{1 + at} \quad \therefore a = \frac{P_t - P_0}{P_0 t}$$

a is the coefficient of the increase of pressure when volume remains constant.

If the pressure remains constant, then—

$$V_0 = \frac{V_t}{1 + at} \quad \therefore a = \frac{V_t - V_0}{V_0 t}$$

a is the coefficient of the expansion of gases (increase of volume) under constant pressure. P is the coefficient already found by Gay Lussac.

If Boyle's and Charles's laws were rigorously true, the two coefficients would be equal. A further examination is due to Regnault.

47. Relation between Pressure, Temperature, and Volume.—Regnault's Method. — (A) *Constant Volume.*—(1) The capacity of a bulb, A (Fig. 38), and stem to a certain mark, a , are accurately determined at 0° and 100° . The stem is calibrated, and therefore the volume of the distance ab is known.

(2) The bulb and stem are filled with dry gas.

(3) The coefficient of expansion of the glass is known.

The stem is fixed into a wider vertical tube, M, which, in turn, is connected with a similar vertical tube, N, open at the top. Mercury can be poured into the top of N or be taken from the apparatus by turning the tap R, when it flows into the vessel D.

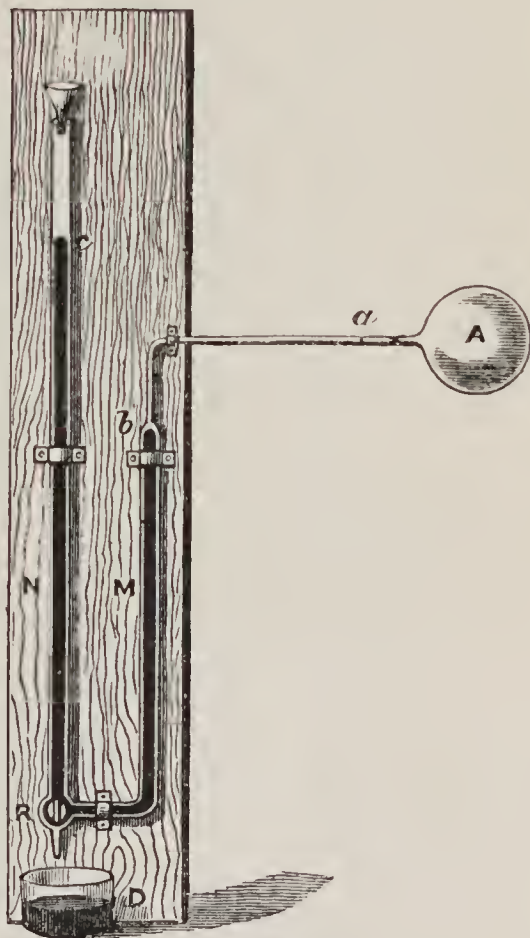


FIG. 38.

The bulb and stem to a are first surrounded with melting ice. By pouring mercury into N, or by running it off at R, it is arranged that the mercury rises to b . Suppose its position in the other tube is c . There is then a mass of imprisoned air, whose volume is V_0 (the bulb and stem to a) at a temperature of 0° C., and v (the stem from a to b) at a temperature of t° , that of the room. This gas is subjected to a pressure of the atmosphere + the pressure due to a column of mercury whose height is the difference of the levels of c and b . Let the sum of these pressures be P . The temperature of the room will be slightly above zero, so that the gas in the tube is subject to a pressure equivalent to $\frac{P}{1 + \Delta t}$ at 0° , where Δ is the coefficient of expansion of mercury. Call this P_0 .

The bulb and stem to a are now surrounded with a steam bath whose temperature is T° , differing but slightly from 100° . The air in the bulb expands; but by pouring mercury into N, the mercury is forced back to the mark b , rising, of course, higher in \bar{N} to some position, c' . The gas is now subject to a pressure, Q , which equals the barometric height + the difference in levels of b and c' . This reduced to $0^\circ = \frac{Q}{1 + \Delta t}$. Call this Q_0 .

The volume of the bulb and stem to a is now $V_0(1 + KT)$, K being the coefficient of cubical expansion of glass. From a to b the volume is v ; this we can assume remains constant during the experiment.

In the first part we have a volume of air, $V_0 + \frac{v}{1 + at}$, pressure P_0 , and temperature 0° C.; in the second part, reducing all to 0° C., there will be a volume—

$$\frac{V_0(1 + KT)}{1 + aT} + \frac{v}{1 + at} \text{ at } 0^\circ \text{ and pressure } Q_0$$

a is the mean coefficient of expansion of dry air for 1°

Applying Boyle's law—

$$P_0\left(V_0 + \frac{v}{1 + at}\right) = \left(\frac{V_0(1 + KT)}{1 + aT} + \frac{v}{1 + at}\right)Q_0$$

a is the only unknown quantity.

Regnault by this method found α , the coefficient of pressure at constant volume, to be 0.003663. Its value in the previous section is given as $\alpha = \frac{P_t - P_0}{P_0 t}$

(B) *Constant Pressure*.—The experiments were repeated, arranging so that the pressure should remain constant. This was attained by seeing that the mercury in the experiments stood at the same level in each tube; the gas was thus subjected to the pressure of the atmosphere. The gas, in expanding, was forced down M, and this being large compared with the bulb, it was necessary to know its exact temperature; M and N were therefore surrounded by a bath of water whose temperature was accurately known.

The calculation was similar to the former, and Regnault found the coefficient of expansion at constant pressure to be $\alpha = \frac{V_1 - V_0}{V_0 t}$; but the value obtained was 0.00367 (cf. § 46).

The following results were obtained:—

		Coefficient of increase of pressure at constant volume.		Coefficient of increase of volume at constant pressure.
Hydrogen	...	0.003667	...	0.003661
Air	...	0.003665	...	0.003670
Nitrogen	...	0.003668	...	0.003670
Carbonic acid	...	0.003688	...	0.003710
Sulphurous acid	...	0.003845	...	0.003903

These numbers were calculated from the dilatation between 0° and 100° C.

Further researches showed that the numbers increased with the pressure; for example, the coefficient of increase of volume of air under constant pressure, at a pressure of 760 mm. was 0.00367; at a pressure of 2620 mm. it became 0.003696.

Sulphurous acid rose from 0.00390 at 760 mm. pressure to 0.00398 at 980 mm. pressure.

Air was examined carefully at constant volume, beginning with various pressures. A given mass of dry air was subjected to a certain pressure, measured in terms of the height of the mercury column above or below the pressure of the atmo-

sphere at 0° C. ; it was then heated to 100° , and the pressure was read after seeing that the gas occupied the original volume. The coefficient of the increase of pressure was then found after necessary calculations and corrections.

Pressure at 0° .		Pressure at 100° .		Coefficient.
109.72		149.31	...	0.003648
266.06	...	395.07	...	0.003654
760.00	...	1038.54	...	0.003665
2144.18	...	2924.04	...	0.003689

The changes in the case of gases that are easily liquefied will be discussed later.

48. Deviations from the Two Gaseous Laws.—(Read §§ 42 and 43.) The following results, taken from Amagat's researches, will show the increased resistance gases offer to compression at high pressure. The temperature was at 15° C. throughout, and in each case the gas occupied unit volume at a pressure of 1 atmosphere. The last column gives the volume a gas would occupy at each pressure, if it obeyed Boyle's law :—

Pressure in atmospheres.	Air.	Nitrogen.	Hydrogen.	Perfect gas.
750	0.00220	0.00262		0.00133
1000	0.00197	0.00203	0.00169	0.00100
1500	0.00171	0.00176	0.00134	0.00067
2000	0.00157	0.00161	0.00116	0.00050
2500	0.00147	0.00151	0.00105	0.00040
3000	0.00140	0.00145	0.00096	0.00030

The deviations from Charles's law are more marked. This is especially the case at high temperatures, when an increase in temperature is followed by a greater increase in volume than the simple form of the law accounts for.

49. Joly's Air-Thermometer.—The coefficient of gases being much higher than that of liquids, and being moreover fairly constant between certain limits, has suggested the use of gases in thermometry. A simple form is shown in Fig. 85 ; the pressure will, however, vary for every position of the fluid, and this leads to calculations for each reading.

The air-thermometer of Joly (Fig. 39) is an adaptation of Regnault's apparatus.

α is a glass bulb with a fine tube bent twice; its volume is V (about 50 c.c. capacity). This is joined to another tube, R , supported by a block, A . R is connected by indiarubber tubing to a longer open tube, R' , supported by a block, A' . R , R' and the indiarubber tube contain mercury. α is filled with dry air and is surrounded with melting ice. R' is raised or lowered until the mercury rises to a fixed mark, S . Then we have a volume V , at temperature 0°C . and pressure P , equal to that of the atmosphere, together with (or less than) that due to the column of mercury whose vertical height is the distance between S and the level of the mercury in R' . Then, neglecting the small portion of the tube not

surrounded with melting ice, $\frac{VP}{T} = \text{a constant, } C$, by Boyle's and Charles's laws. This first measurement gives C when necessary.

If now the bulb be placed in an enclosure whose temperature is t° , the column of the glass becomes $V(1 + Kt)$, where K is the coefficient of the cubical expansion of glass. The total pressure, p , is noted as before, after the mercury is brought to the level S by raising or lowering R' . If a be the coefficient of expansion of air, then—

$$\frac{V(1 + Kt)p}{1 + at} = \frac{VP}{1}$$

$$\therefore 1 + at = \frac{p}{P}(1 + Kt)$$

This is the same formula as in § 47, omitting slight corrections, and Joly, by his apparatus, determined the coefficient of expansion, a . Also—

$$t = \frac{p - P}{aP - Kp}$$

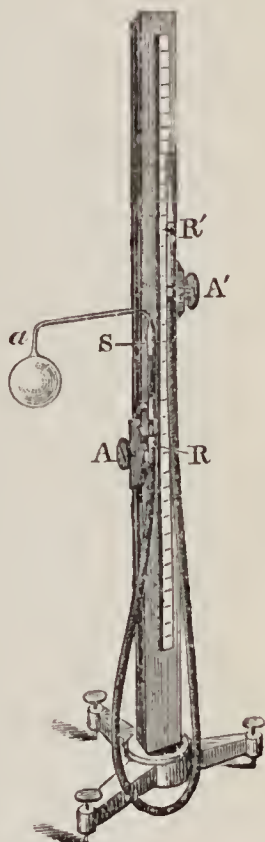


FIG. 39.

Substituting the accepted values of α and K , and determining P for the particular thermometer, then—

$$t = \frac{p - P}{0.003665P - 0.000025p}$$

i.e. the temperature is determined from the pressure p .

50. Density of Gases.—The density of a substance is the mass of unit volume.

If V be the number of units of volume in a substance, D the density, then—

$$VD = \text{mass} = m$$

If the volume changes to V_1 , and the density to D_1 , then—

$$VD = m = V_1D_1 \quad \therefore \frac{V}{V_1} = \frac{D_1}{D}$$

i.e. the density is inversely as the volume. Also, if T be the temperature measured from absolute zero—

$$\begin{aligned} \frac{VP}{T} &= \frac{V_1P_1}{T_1} & \therefore \frac{V}{V_1} &= \frac{D_1}{D} = \frac{P_1T}{PT_1} \\ \therefore \frac{P}{DT} &= \frac{P_1}{D_1T_1} = \frac{P_2}{D_2T_2} = \text{etc.} = \text{constant} \\ \text{and } D &= \frac{P}{T} \times \text{constant} \end{aligned}$$

or density varies directly as the pressure and inversely as the absolute temperature. Therefore, in dealing with densities, the pressure and temperature must be considered. This is especially the case in gases.

In liquids, the temperature must be allowed for; the effect of pressure, however, is small and can generally be neglected. In solids, while temperature must be considered in accurate calculations, the effect of pressure can generally be neglected.

51. Density of Gases.—Regnault's Method.—The specific gravity of the gas is determined relative to air.

Two globes made of the same kind of glass, as nearly equal in volume as possible, and each of about 10 litres capacity, were used.

(1) Experiments were made to ensure that the two globes

were of equal volume, so that on hanging them from the two arms of a balance, equal volumes of air were displaced, and the corrections for weighing in air were unnecessary.

(2) One globe was placed in melting ice (Fig. 40). A three-way stop-cock, A, enabled the globe to be connected either with an air-pump or with drying-tubes, M N, through which the gas entered by C. The following operations are

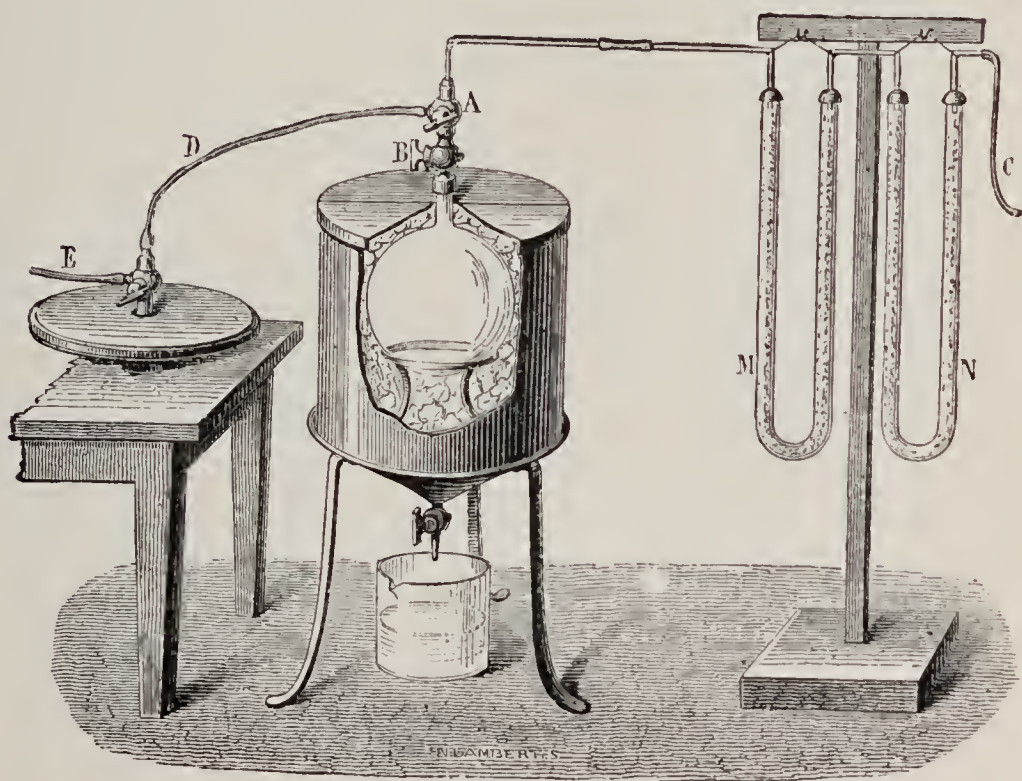


FIG. 40.

performed: the air is exhausted through D; then A is turned so that dry gas enters through M N while D is shut off. The drying-tubes are shut off, and the air and gas are again drawn off; this is repeated until the globe contains dry gas only, without any admixture of air. The gas is now exhausted as far as possible, until the pressure (measured by a differential barometer connected by E) becomes small: let this pressure be p .

B is closed; the globe is removed, cleaned, and weighed, with the other globe as a counterpoise. Shot is placed in the scale of B until there is a perfect balance. The globe contains a mass of gas whose volume is V , at temperature 0° C., and pressure p millimetres of mercury.

The globe is now replaced in melting ice. The stop-cock is turned so that dry gas enters through M and N; the stop-cock is kept open until the gas is at the pressure of the atmosphere, P , read from the barometer. B is closed, and, in a similar manner to the above, a perfect balance is made by adding a weight, m , to the other scale. m is the mass of the gas that has entered during the second operation, that is, it is the mass of a volume, V , at temperature 0°C. , and pressure $(P - p)$ millimetres of mercury. An equal volume of the gas at standard pressure would weigh—

$$m \frac{760}{P - p}$$

Exactly similar operations are repeated for dry air, and a weight, m' , is obtained which is the mass of a volume of dry air (V) at temperature 0°C. and under a pressure $(P' - p')$. The mass of this volume at standard pressure would be—

$$m' \cdot \frac{760}{P' - p'}$$

The specific gravity of the gas, compared with air under similar conditions, is—

$$\frac{m \cdot \frac{760}{P - p}}{m' \cdot \frac{760}{P' - p'}} = \frac{m(P' - p')}{m'(P - p)}$$

The following relative densities of gases have been obtained by this method:—

Air	1.00000	Hydrogen ...	0.06926
Oxygen	1.10563	Carbonic acid ...	1.52901
Nitrogen	0.97137		

If the density of air were known at the normal temperature and pressure, the density of any gas whose specific gravity is known could be at once calculated. In the above experiments the weight of a certain volume, V , of air at 0°C. and 760 mm. pressure has been found to be—

$$m' \cdot \frac{760}{P' - p'} = M$$

The density, $D = \frac{M}{V}$. It is therefore necessary to determine the exact volume of the globe under similar conditions of temperature and pressure.

(1) The globe is filled (observing the former precautions) with dry air at a temperature 0° C. and pressure P . It is weighed without using the second globe as a counterpoise. The weight m gives the mass of the globe and the air under the above conditions.

(2) The globe is filled with water, a method analogous to filling a thermometer being followed. A curved tube is fitted to the globe, one end dipping under boiling water; on heating the globe to expel some of the air, and allowing the globe to cool, part of the water is forced over into the globe; this is boiled, the air is chased out, and on cooling the boiling water siphons over. The globe after cooling is placed in melting ice for twenty-four hours; the stop-cock is closed, the globe cleaned and left for several hours in a room whose temperature is below 9° . It is weighed in this room again without the balancing globe. If the weight is m' , the barometer being P' —

$$m' - m = (\text{weight of globe} + \text{water}) - (\text{weight of globe} + \text{air})$$

$$= \text{weight of water} - \text{weight of air}$$

i.e. the weight of water, $W = m' - m + \text{weight of air}$.

The weight of air is M (see above), it being found that the correction for the expansion of glass and air, and for the air displaced in weighing, could be neglected.

Thus the weight of water at 0° which the globe at 0° would contain is known. Unit volume of water at $4^{\circ} = 1.000017$ at

0° C., *i.e.* 1 cubic centimetre of water at 0° weighs $\frac{1}{1.000017}$ gram; or 1.000017 c.c. at 0° weighs 1 gram. Therefore W , the weight of water obtained above in grams, represents a volume, $W \times 1.000017$ c.c. Call this V , a quantity which now is known.

(a) The mass of the air is known (M).

(b) The volume of this air is known (V).

\therefore the density of dry air = the mass of 1 c.c. = $M \div V$ can be calculated

This was found to be 0.001293187 gram.

1 litre (1000 c.c.) of dry air at 0° C. and pressure of 760 mm. of mercury, weighs 1.2932 gram.

In the following table the first column gives the absolute density of the gas, that is, the mass of 1 c.c. at 0° C. and at 760 mm. pressure; the second column gives the relative density compared with air under similar conditions; the third the relative density compared with hydrogen:—

	Density.	Air = 1.	Hydrogen = 1.
Air ...	0.0012932	1.0	14.438
Oxygen ...	0.0014298	1.1056	15.96
Hydrogen ...	0.0000896	0.0693	1.0
Nitrogen ...	0.0012561	0.9714	14.0
Carbonic acid ...	0.0019774	1.5290	22.0
Marsh-gas ...	0.0072700	0.5590	8.0
Ammonia ...	0.0076970	0.5910	8.5

52. Boyle's and Charles's Laws.—Special Case.—

In the case of air, if the units be 1 foot and 1 lb., and the temperature scale that of Fahrenheit, we have the following experimental results:—

1 lb. of air at 32° F. and at normal atmospheric pressure of 14.7 lbs. per square inch, or 2116.8 lbs. per square foot, measures 12.387 cubic feet.

$$\therefore \frac{PV}{T} = \text{constant} = \frac{2116.8 \times 12.387}{492.6} = \frac{P_1 V_1}{T_1}$$

$$\therefore \frac{P_1 V_1}{T_1} = 53.2$$

\therefore at any absolute temperature T_1 —

$$P_1 V_1 = 53.2 T_1$$

If, therefore, any two of the quantities P , V , T , be known, the third can be readily calculated.

If a number of calculations are needed for hydrogen or other gas, we again determine P and V at some known temperature.

1000 c.cm. of hydrogen at 0° C. and 760 mm. pressure
= 0.089578 gram

If the units be 1 centimetre, 1 gram, and 1° C.—

$$1 \text{ gram} = \frac{1000}{0.089578} = 11163.45 \text{ c.c.}$$

A column of mercury 760 mm. high will exert a pressure of 1033.296 grams per square centimetre.

$$\frac{p_0 v_0}{T_0} = \frac{1033.296 \times 11163.45}{273} = 42217$$

$$\therefore p v = 42217 T$$

53. Gases at Normal Temperature, T_0 (0° C.), and Pressure, P_0 (760 mm.).—The necessary instructions for changing the volumes of gases at any temperature and pressure to the normal temperature and pressure have already been given (§ 46). It is, however, necessary, on account of the importance of the change, to again examine the process.

Let the volume be V_t in c.cm., the pressure P_t in millimetres of mercury, and the temperature t° C.

(1) Let the pressure remain constant at P_t , while the temperature changes to 0° , then the new volume $V = \frac{V_t}{1 + at}$ by Charles's law.

(2) Let the pressure change from P_t to P_0 , the temperature remaining at 0° C. If V_0 be the new volume—

$$V P_t = V_0 P_0$$

$$\therefore V_0 = V \cdot \frac{P_t}{P_0} = \frac{V_t \cdot P_t}{(1 + at) P_0}$$

a = coefficient of expansion = 0.003665 for all gases; $P_0 = 760$

$$\therefore V_0 = \frac{V_t \cdot P_t}{(1 + 0.003665t) \cdot 760}$$

WORKED EXAMPLES.

1. The volume for a certain quantity of air at 50° C. is 500 cubic inches. Assuming no change of pressure to take place, determine its volume at -50° C. and at 100° C. respectively.

$$\frac{p_1 v_1}{T_1} = \text{constant} = \frac{p_2 v_2}{T_2}$$

\therefore pressure is constant, $\therefore p_1 = p_2$

$$\therefore \text{volume at } -50^{\circ} \text{ C.} = v_2 = v_1 \frac{T_2}{T_1} = 500 \cdot \frac{273 - 50}{273 + 50} = \frac{500 \times 223}{323} \\ = 345.2 \text{ cubic inches}$$

$$\text{Volume at } 100^{\circ} \text{ C.} = v_2 = 500 \cdot \frac{373}{323} = 577.4 \text{ cubic inches}$$

Or, since pressure is constant by Charles's law, the volumes vary as the absolute temperature.

$$\therefore \frac{\text{volume at } -50^{\circ}}{\text{volume at } 50^{\circ}} = \frac{273 - 50}{273 + 50} = \frac{223}{323}$$

$$\therefore \text{volume at } -50^{\circ} = \text{volume at } 50^{\circ} \times \frac{223}{323} \\ = 500 \times \frac{223}{323} \\ = 345.2 \text{ cubic inches}$$

2. A quantity of gas collected in a graduated tube over mercury measures 305.6 c.cm.; the mercury in the tube is 47 mm. above the level in the dish; the temperature of the room is 15° C. , and the barometer reads 762 mm. : find the volume of gas at 0° C. and 760 mm. pressure.

The 305.6 c.cm. is subjected to a pressure of $762 - 47 = 715$ mm. of mercury.

$$(1) \text{ Its volume when the pressure is 760 mm.} = 305.6 \times \frac{715}{760} \text{ at } 15^{\circ}$$

$$(2) \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad 760 \text{ mm. and the temperature is } 0^{\circ} \text{ C.} \\ = \frac{305.6 \times 715}{760 \times (1 + 0.003665 \times 15)} = \text{etc.}$$

Or, by using the formula in § 53—

$$\text{Volume} = \frac{V_t \cdot P_t}{(1 + 0.003665 t) 760} = \text{as before}$$

3. A glass flask was filled with dry air when the temperature of the room was 10° C. and the barometer read 750 mm. The stop-cock was closed and the flask weighed. It was now placed in a bath of water at 100° C. The stop-cock was opened, afterwards closed, and when the flask cooled down it was again weighed. It was found that 2 grams of air had escaped. Find the capacity of the flask at 10° C. and at 0° C. (coefficient of cubical expansion of glass = 0.000025).

Let v_0 , v_{10} , v_{100} = volume of flask at 0° , 10° , and 100° C. in c.cm.

$$v_{10} = v_0(1 + 0.00025) = \text{volume of air at } 10^{\circ}$$

$$v_{100} = v_0(1 + 0.0025)$$

The volume of air at 10° is v_{10} ; this becomes—

$$v_{10} \left(\frac{273 + 100}{273 + 10} \right) = v_{10} \frac{373}{283} \text{ at } 100^{\circ} \\ = v_0(1.00025) \frac{373}{283}$$

$$\therefore \text{the air that escapes} = v_0(1.00025 \frac{373}{283} - 1.0025)$$

$$= \frac{v_0}{283}(89.3857) \text{ c.cm.}$$

Dividing this by the density of air at 100° , that is, $0.001293 \times \frac{273}{373}$ we get the mass of this air. This equals 2 grams.

$$\therefore 2 \text{ grams} = v_0 \cdot \frac{89.3857 \times 373}{283 \times 273 \times 0.001293} = \frac{v_0 \times 89.3857}{283} \times \frac{0.001293 \times 273}{373}$$

$$\therefore v_0 = \frac{2 \times 283 \times 273 \times 0.001293}{89.3857 \times 373} = \text{Ans. in c.cm.}$$

v_{10} equals this quantity multiplied by 1.00025

$$v_0 = \frac{2 \times 283 \times 273 \times 76}{89.3857 \times 0.001293 \times 273 \times 75} = 67.80 \text{ cc}$$

EXAMPLES. III.

1. Explain clearly the difference between real and apparent expansion of a liquid. What quantity do you neglect in stating that $\Delta = D + G$?

If the coefficient of cubical expansion of the solid were 0.003, and the coefficient of apparent expansion of the liquid were 0.04, would the above formula be true? Find, under these conditions, the coefficient of absolute expansion of the liquid.

2. A glass flask contains when full at 0°C . 100 c.cm. of mercury. The coefficient of cubical expansion of glass being 0.000026, and that of mercury 0.00018, find the volume at 100°C . of the mercury driven out when the flask and mercury are heated to 100° . (London Matric., 1885.)

3. The barometer is read as 764.5 mm. in a laboratory when the temperature is 12°C . State, in order of their importance, the corrections that should be made.

4. How would you determine the coefficient of apparent expansion and of absolute expansion of glycerine?

5. Water at 60°F . is exposed to air at 30°F .; it gradually cools until it reaches the temperature of the air: describe fully the changes which occur in the water during the whole process of cooling.

6. Describe Dulong and Petit's method of determining the absolute expansion of mercury.

In an experiment one tube was at 0°C ., the other was at 150° ; the heights of the columns of mercury were 36.00 inches and 36.97 inches: calculate the coefficient of absolute expansion of mercury.

7. State exactly in what respects Regnault's method was an improvement upon Dulong and Petit's method.

8. State clearly the meaning of "mean coefficient of expansion" and "true coefficient of expansion."

9. Represent graphically the results of the tables on pp. 45 and 50

EXAMPLES. IV.

1. What relation exists between the temperature, pressure, and volume of a given quantity of gas? A cubic foot of air at 100°C . is cooled down to 0° , and at the same time its pressure is halved: determine its new volume. $(a = \frac{1}{273})$

2. Describe Regnault's experiments and apparatus to determine the coefficient of expansion of a mass of air under constant pressure; and state the conclusion that he drew from the fact that it differs from the coefficient of increase of elasticity under constant volume.

3. If a litre of air at 0°C . and a pressure of 76 cm. of mercury has a mass of 1.293 gram, determine the mass of a cubic metre of air measured at 50°C . and a pressure of 50 cm.

4. Describe a method of finding the coefficient of increase of elasticity of a mass of air occupying a constant volume.

5. A solid at 0°C ., when immersed in water, displaces 500 cubic inches: at 30°C . it displaces 503 cubic inches: find its mean coefficient of linear expansion. (London Matric., 1880.)

6. A drying-oven measures internally 20 cm. \times 18 cm. \times 15 cm.; the temperature is 120°C .; the barometer reads 750: find the mass of air contained in the oven.

7. 10 cubic feet of dry air measured at 32°F . when the barometer is 29 inches are forced into a globe whose diameter is 10 inches; the globe is heated to the temperature of steam at normal pressure: find the pressure inside the globe.

8. 10 grams of nitrogen are forced into a vessel whose capacity is 1000 c.c., the temperature being 17°C .: find the pressure on the vessel.

9. What is an isothermal? Apply your answer to graphically representing Boyle's law.

10. State any deviations you know from Boyle's law.

11. Find the absolute density of dry air at 0°C . and 76 cm. pressure from the following data, obtained by Regnault by his compensation method:—

When the globe was filled with dry air at 0°C . and 76.199 cm. pressure, and 1.487 gram added, they equilibrated the compensation globe and the counterpoise. After being placed in melting ice, and exhausted till the pressure of the residual air was 0.843 cm., the globe and its contents, together with 14.151 grams, equilibrated the compensation globe and its counterpoise. At 6°C . and 76.177 cm. pressure the globe, when open, weighed 1258.55 grams.

When it was filled with water at 0°C ., and weighed at 6°C . and 76.177 cm. pressure, it weighed 11,126.06 grams. (Day's Examples.)

CHAPTER V.

HEAT AS A QUANTITY.

54. Unit of Heat.—In the previous chapter the change in temperature alone has been observed. Heat has been given to or taken away from substances, but there has been no attempt made to measure the amount.

A certain quantity of heat is required to raise the temperature of 1 lb. of water from 0° to 1° C. ; under the same conditions this quantity of heat will always raise 1 lb. of water from 0° to 1° C. ; if the temperature under the same conditions fall from 1° to 0° C., then an equal quantity of heat will be liberated. If we experiment with 2 lbs. of water, we shall deal with twice the amount of heat ; or, with 10 lbs. of water, ten times the original amount of heat.

Assuming for the present, what is nearly true, that the same amount of heat is required to raise the temperature of 1 lb. of water through 1° , beginning at 0° , 1° , 2° , 10° , 60° , etc., we can state that it would take six times the amount of heat to raise 1 lb. of water from 0° to 6° that it takes to raise 1 lb. from 0° to 1° ; and fifty times the amount to raise 5 lbs. from 50° to 60° that it takes to raise 1 lb. from 0° to 1° .

It is also assumed that the amount of heat necessary to raise a given mass of a substance through a given range of temperature equals the amount of heat liberated when the given mass cools from the higher to the lower temperature.

Heat, then, is a measurable quantity. It is necessary to decide upon a unit, the particular unit selected being a matter of convenience.

In England the unit of heat, or thermal unit, is the amount

of heat required to raise 1 lb. of water under the pressure of one atmosphere from 50° to 51° Fahrenheit.

For practical purposes the effect of pressure on water can be neglected, and the specification of the particular temperature is unnecessary, and the unit of heat becomes the quantity of heat required to raise the temperature of water through one degree. The other particulars should, however, always be understood.

For scientific purposes the unit of heat is the amount of heat required to raise 1 gram of water under a pressure of one atmosphere from 0° to 1° Centigrade.

In the following calculations it will be assumed that the unit of heat is the amount required to raise 1 gram of water through 1° Centigrade; that is, that the small variation due to change of atmospheric pressure and due to temperature will be neglected.

If 5 lbs. of water at 0° be mixed with 5 lbs. of water at 100° , the result is 10 lbs. at 50° ; the former has taken up 250 units, the latter has given up 250 units. 10 lbs. of water at 0° + 20 lbs. at 30° = 30 lbs. at 20° ; the former has taken (10×20) units of heat that have been disengaged from the 20 lbs. cooling 10° and giving up 200 units.

Generally, if a mass m_1 of water at t_1° be mixed with a mass m_2° at t_2° (a higher temperature), the resulting temperature will be θ ; so that—

$$m_1(\theta - t_1) = m_2(t_2 - \theta)$$

$$\therefore \theta = \frac{m_2 t_2 + m_1 t_1}{m_2 + m_1}$$

55. Specific Heat.—On mixing 1 lb. of turpentine at say 15° C. with 1 lb. of water at 100° C., the result is a mixture of 2 lbs. at about 75° C.; *i.e.* 1 lb. of turpentine has been heated through 60° C. by 25 units of heat.

To raise 1 lb. of turpentine 1° requires, then, 0.42 unit of heat nearly.

The ratio of the quantity of heat required to raise a given mass of the substance at any given temperature through one degree, to the quantity required to raise an equal mass of

water through the same range of temperature, is called the specific heat of the substance at that temperature.

Specific heat is a ratio, and therefore does not depend upon any particular kind of units. Numerically, it is equal to the thermal units required to raise a unit of mass of the substance through 1° of temperature, and is sometimes defined as such.

In the above experiment the mass in each is 1 lb.

$$\therefore \text{specific heat of turpentine} = \frac{25}{60} = 0.42$$

If 2 lbs. of iron at 100° C. be mixed with 5 lbs. of water at 10° C., the resulting temperature will be about 14° C.

To raise the temperature of 5 lbs. of water from 10° to 14° requires 5×4 thermal units ;

2 lbs. of iron cooling 86° , *i.e.* $(100 - 14)^\circ$, give up 20 thermal units ;

\therefore 2 lbs. of iron cooling 1° give up $\frac{20}{86}$ thermal units ; *i.e.* 0.24 thermal unit nearly

$$\begin{aligned} \therefore \text{specific heat of iron} &= \frac{\text{heat required to raise 2 lbs. of iron } 1^\circ}{\text{heat required to raise 2 lbs. of water } 1^\circ} \\ &= \frac{20}{86} \div 2 = 0.12 \end{aligned}$$

The following experiments roughly show that the specific heats of substances vary :—

Take discs of silver (a florin), copper (a penny), iron, lead, same size and thickness ; hold them at equal distances from a bright fire ; in one minute test the temperature of each with a thermometer. Their order as regards temperature is—lead, silver, copper, iron. All have approximately received equal amounts of heat, and we infer that the specific heat of iron, for example, is greater than that of lead. (To make the experiment more exact, equal masses should be taken, that is, the thicknesses of the discs should vary inversely as the densities.)

Weigh into three separate test-tubes two ounces of iron shot, two ounces of finely granulated zinc, two ounces of

mercury ; place the test-tubes in a beaker of boiling water, and let them remain some time. Weigh into three separate beakers two ounces of water, and observe the temperature. In an experiment it was 16° C. Remove the test-tubes and pour the contents (at 100° C.) into the separate beakers ; stir, and note as carefully as you can the final temperature.

(a) Mercury and water, final temperature = 19°

(b) Zinc " " " " = 23°

(c) Iron " " " " = 25°

\therefore 2 ozs. of mercury cooling 81° heat 2 ozs. of water 3°

2 " zinc " 77° " 2 " " 7°

2 " iron " 75° " 2 " " 9°

\therefore 2 ozs. of mercury cooling 1° heat 2 ozs. of water $\frac{1}{27}^{\circ}$

2 " zinc " 1° " 2 " " $\frac{1}{11}^{\circ}$

2 " iron " 1° " 2 " " $\frac{1}{8\frac{1}{3}}^{\circ}$

\therefore specific heats of water, iron, zinc, mercury, are as—

$$1 : \frac{3}{25} : \frac{1}{11} : \frac{1}{27}$$

If m , s , t , represent the mass, specific heat, and temperature of a substance ; and M , S , T , represent the mass, specific heat, and temperature of water (S , of course, = 1) ; and if θ be the final temperature after mixing the substance and the water —

$$ms(t - \theta) = MS(\theta - T)$$

$$\therefore s = \frac{MS}{m} \cdot \frac{\theta - T}{t - \theta}$$

$$= \frac{M}{m} \cdot \frac{\theta - T}{t - \theta}$$

It is assumed, in the above calculations, that all the heat given up by the substance is used in heating the water.

The specific heat of substances can be roughly determined by using a beaker or a thin copper vessel as the calorimeter.

Solids should be in strips and wound into a spiral shape, so that they may the more readily give up their heat. By attaching them to a fine piece of thread and suspending them in steam they can be raised to 100°C . The temperature of a weighed quantity of water in the calorimeter is taken, the solid is rapidly introduced, the whole stirred, and the final temperature read.

It is obvious that there are several sources of error. Heat is lost on moving the solid, part is used in heating the calorimeter and thermometer, and part is lost by radiation.

56. Thermal Capacity.—If s be the specific heat of a substance whose mass is m , and θ be the range of temperature through which it is heated—

Then to raise m units water through θ° would req. $m\theta$ therm. units

$$\begin{array}{ccccccc} \therefore & , & m & , & \text{substance} & , & \theta^{\circ} & , & ms\theta & , \\ \therefore & , & m & , & & , & 1^{\circ} & , & ms & , \end{array}$$

i.e., if Q be the quantity of heat—

$$Q = ms\theta$$

$\frac{Q}{\theta}$ is called the thermal capacity of the substance: it is the heat required to raise the temperature of the substance through one degree.

For example, the quantity of heat necessary to raise 8 lbs. of turpentine through 15° is—

$$Q = 8 \times 0.42 \times 15 = 50.4 \text{ thermal units}$$

It is sometimes inconvenient or unnecessary to separate m and s . Thus we might find by experiment the quantity of heat necessary to raise a mass of turpentine through 15° . Suppose the quantity was 50.4 thermal units. Then to raise this mass of turpentine through 1° would require 3.36 units.

Then 3.36 units would be the mean thermal capacity of the substance through the given range. If, in addition, we knew that the mass was 8 lbs., then $\frac{3.36}{8} = 0.42$ is the thermal capacity of unit mass. This is numerically equal to the specific heat.

The expression, “thermal capacity of unit volume,” is also in use; it is the product of the specific heat and the density.

57. Water Equivalent.—The thermal capacity of a substance is the product of its mass and specific heat, $m \times s$. It represents the number of thermal units required to raise its mass through one degree. Now, if we take a mass of water, ω , numerically equal to $m \times s$, then it will take the same quantity of heat to raise m units of the given substance through one degree as it takes to raise ω units of water through one degree.

ω is called the water equivalent of the substance, seeing that calculations will not be affected if we imagine the substance removed, and ω units of mass of water substituted for it.

58. The Method of Mixtures.—Specific heats are frequently determined by the method of mixtures. Easy examples have already been given.

If m_1, s_1 , and t_1 represent the mass, specific heat, and temperature of a given body; and m_2, s_2 , and t_2 the mass, specific heat, and temperature of a second body; then, if they be mixed and no heat enters or escapes, and if the heat given up by one be wholly used in heating the other, they finally assume a common temperature, θ . The hotter body has fallen from t_2 to θ , and the colder has risen from t_1 to θ . The former has lost $m_2 s_2 (t_2 - \theta)$ units of heat; the latter has gained $m_1 s_1 (\theta - t_1)$ units. These are equal.

$$\therefore m_1 s_1 (\theta - t_1) = m_2 s_2 (t_2 - \theta)$$

$$\therefore \theta = \frac{m_1 s_1 t_1 + m_2 s_2 t_2}{m_1 s_1 + m_2 s_2}$$

$$\text{also } s_1 = \frac{m_2 s_2 (t_2 - \theta)}{m_1 (\theta - t_1)}$$

$$\text{and } s_2 = \frac{m_1 s_1 (\theta - t_1)}{m_2 (t_2 - \theta)}$$

If there be three substances, we have—

$$m_1 s_1 (\theta - t_1) + m_2 s_2 (\theta - t_2) = m_3 s_3 (t_3 - \theta)$$

$$\therefore \theta = \frac{m_1 s_1 t_1 + m_2 s_2 t_2 + m_3 s_3 t_3}{m_1 s_1 + m_2 s_2 + m_3 s_3}$$

$$\text{and } s_3 = \frac{m_1 s_1 (\theta - t_1) + m_2 s_2 (\theta - t_2)}{m_3 (t_3 - \theta)}$$

The heating of the surrounding vessel and the heating of the thermometer cannot be neglected in practice. The experiment is carried out as follows:—

59. The Calorimeter.—The vessel, a cylinder of copper, E (Fig. 41), is suspended inside a similar though larger cylinder, F, by threads, in order to prevent, as far as possible, loss of heat by conduction. The outside of the former and the inside of the latter are highly polished, the aim being

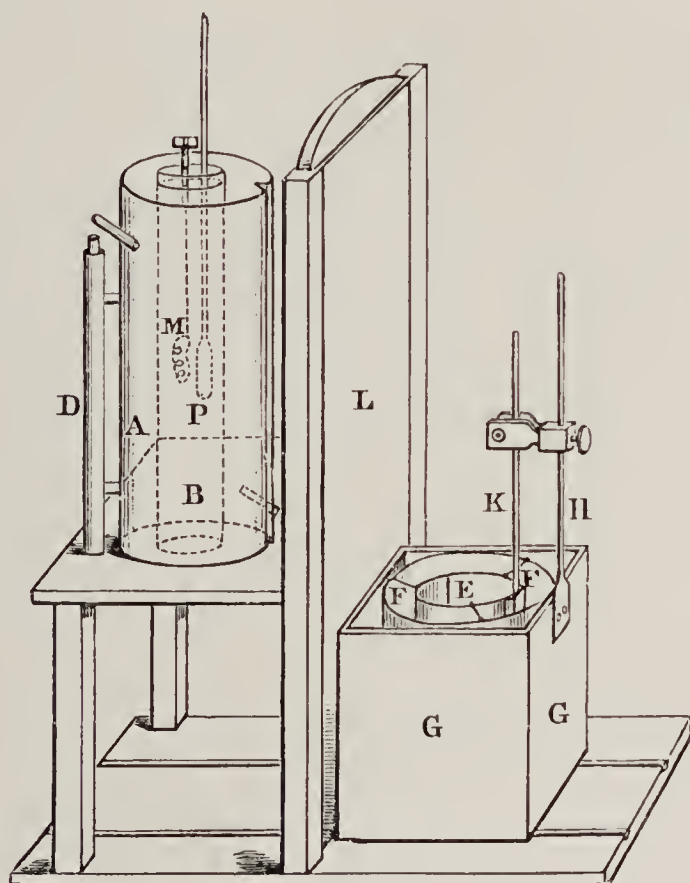


FIG. 41.

to ensure that, if any heat be radiated by the inside vessel, as much as possible shall be reflected by the outside vessel. The vessels are placed inside a wooden box, G, and are packed in felt to prevent variation in the temperature of the surrounding space from affecting the calorimeter. A weighed quantity of water, m , is placed in E, and the temperature t is read from the thermometer K, which is secured to the stand H. Neglecting the water equivalent, we have the simple arrangement of § 55.

To heat the substance, say a small cylinder of iron or copper (if possible the solid should be in spiral form, the better to give up its heat), it should be exposed for some time to steam under ordinary atmospheric pressure. This can be done in the usual steam-jacket modified as follows: A closed copper vessel, A, has a cylinder, B, passing through it; steam enters from a boiler by the lower side tube, and escapes by the upper side tube into a condenser. The central cylinder is closed at the top by a cork. A thermometer, P, passes through the cork, and the solid, M, is suspended by a very fine thread that also passes through the cork. The heater revolves around D, and ordinarily the bottom of B is closed by moving A so that it rests upon the solid board of the stand. The enclosure is then at a temperature, t_2 , very near 100°C . When A is in the position of the figure, it is over a circular aperture cut in the board whose diameter is equal to that of B.

To transfer the solid to the calorimeter with as little loss of heat as possible, the following combined arrangement is made:—

The calorimeter box slides on along two wooden rails, and, by lifting the door L, can be quickly slid into position. When the temperature of the heater is constant, L is raised, the calorimeter is slid beneath the hole in the stand, the heater is brought over the hole, the solid quickly lowered, and the calorimeter is then replaced in its first position, stirred by its thermometer, and the highest point reached by the thermometer noted.

In order to correct for the heat that raises the temperature of the calorimeter and the thermometer, the water equivalent is first determined. This is done by (a) weighing the calorimeter, placing water in the calorimeter; and (b) weighing again, noting the temperature, and then adding a quantity of water at about 30° , stirring, and noting the final temperature; and (c) weighing again. $b - a$ gives the mass m of water at t° , the temperature of the room; $c - b$ gives the mass of water m_1 added at t_1° . Let θ° be the final temperature. Since the heat from a mass m_1 , in cooling from t_1° to θ° , is used in heating

a mass m from t° to θ° , and also in heating the calorimeter and thermometer from t° to θ° , we have—

$$m_1(t_1 - \theta) = m(\theta - t) + \omega(\theta - t)$$

where ω is the water equivalent.

$$\therefore \omega = \frac{m_1(t_1 - \theta)}{\theta - t} - m$$

The water equivalent could be calculated if we knew the mass of the calorimeter, μ , the specific heat of its substance, σ ; and the mass, μ_1 , and specific heat of the thermometer, σ_1 . Then—

$$\omega = \mu\sigma + \mu_1\sigma_1$$

The determination by actual experiment, conducted as far as possible under similar conditions as to temperature as in determining the specific heats, is, however, to be preferred.

In determining the specific heat of a substance of mass m_2 , if s_2 be the specific heat, and t_2 the temperature to which it is heated, then, if m be the mass of water in the calorimeter at t° , and ω be the water equivalent, and θ the final temperature, we obtain, as in § 58—

$$m_2s_2(t_2 - \theta) = (m + \omega)(\theta - t)$$

$$\therefore s_2 = \frac{(m + \omega)(\theta - t)}{m_2(t_2 - \theta)}$$

In determining the water equivalent, the final temperature should, as far as possible, approximate to the final temperature in determining the specific heats. There will be, despite these precautions, a loss due to radiation in determining the specific heat of a substance. This is reduced, if Rumford's method be followed, of arranging the experiment so that the original temperature of the water in the calorimeter be as far below the temperature of the room as the final is above it. During the first part of the experiment the calorimeter will receive heat from the room; during the latter part it will give up heat to the room; these two quantities are nearly equal.

The specific heat of liquids can be found by enclosing them in a thin glass vessel of known mass and known specific heat

—preferably the vessel should be hermetically sealed—heating as before, and allowing for the heating of the glass; or by using the liquid instead of water in the calorimeter, and heating and dropping in a mass of metal of known specific heat.

For example, if m be the mass of the solid, s its specific heat, m' and s' mass and specific heat of the liquid—

$$ms(t - \theta) = m's'(\theta - t') + w(\theta - t')$$

where all is known save s' .

It is supposed in all cases that no chemical action takes place, and that the substance does not dissolve; for example, for substances soluble in water some other liquid in which they are insoluble must be used.

The apparatus Fig. 41 is practically that of Regnault.

60. Latent Heat of Fusion.—By mixing 1 lb. of ice at 0° with 1 lb. of water at 80° C., we obtain 2 lbs. of water at 0° ;

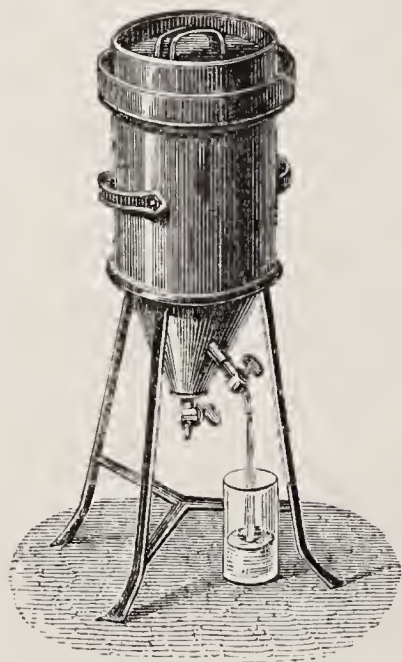


FIG. 42.

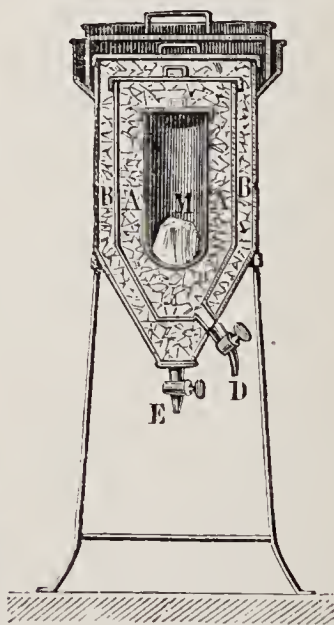


FIG. 43.

that is, 80 thermal units are needed to change 1 lb. of ice at 0° into water at 0° . This is called the latent heat of fusion. It will be discussed later, and is introduced here in order that the following calorimeters may be understood.

61. Lavoisier and Laplace's Calorimeter.—The calorimeter A is placed inside a vessel, B, from which it is separated by melting ice (Figs. 42 and 43). B, in its turn, is inside an

outer vessel, and is also packed in ice. The result is that the ice between A and B cannot be melted by any heat from the outside. The mass M , whose specific heat (s) is to be determined, is raised to a known temperature, t , and is placed in A, and the lids are replaced. M , cooling to 0° C., melts ice between A and B. The water drains off by D, and is weighed. If m be the mass of ice at 0° melted to water at 0° , then—

$$Mst = 80m$$

$$\therefore s = \frac{80m}{Mt}$$

The defects are grave: it is practically impossible to work with small amounts, and even with large masses it is impossible to drain off the whole of the water.

62. Bunsen's Calorimeter.—Ice floats on water. It is therefore less dense, and, in melting, the water formed occupies a less volume than the ice.

A glass vessel, A B C, has a thin glass test-tube, D, fused into it (Fig. 44). A is filled with distilled water that has been

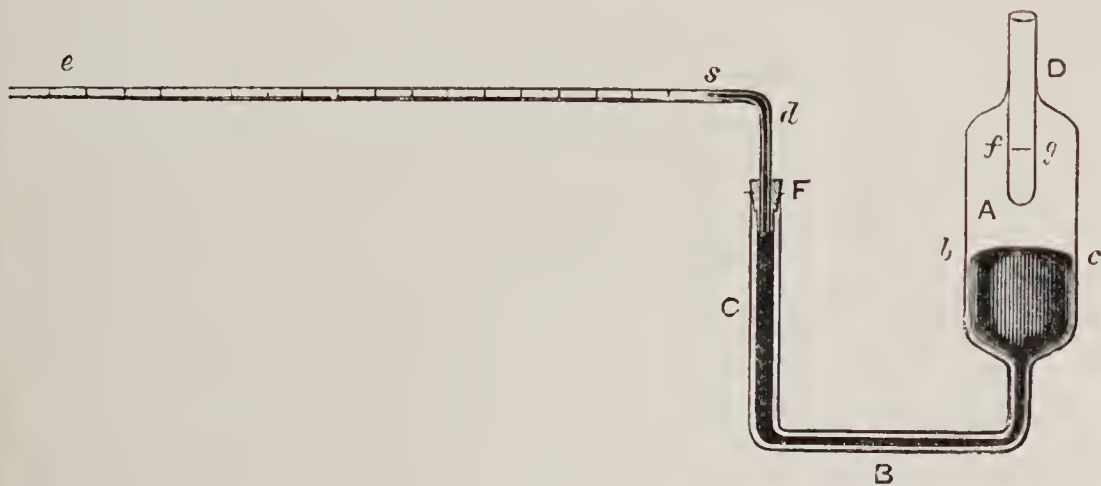


FIG. 44.

thoroughly boiled, by a method that is practically that of filling a thermometer. Then mercury is allowed to enter by the opening at C, and, by tilting, it is arranged that the mercury rises to $b\ c$, the water being above. The mercury must be freed from water and air. The narrow tube $d\ e$ is inserted into C by a cork, F, the mercury rises and flows along $d\ e$. $d\ e$ has been carefully calibrated along its horizontal part. The whole apparatus, which must be free from all bubbles of air, is now

placed in melting ice or snow, and left until its temperature falls to zero. It is now necessary to freeze part of the water surrounding the tube D. The water, being free from air, is somewhat difficult to freeze. The freezing can be readily accomplished by passing through D a current of alcohol previously cooled by a mixture of ice and salt.

The whole, save the tube de , is surrounded with melting ice.

By moving the cork F it is arranged that the mercury reaches a fixed point, e ; a known quantity of water at a known temperature is poured into the test-tube D, and a cork is inserted. The water, on cooling to 0° , melts some of the ice surrounding D, there is a consequent contraction, and the column moves to s , say. s and e can be carefully observed with a telescope. Let se be n divisions; then a mass of water m has cooled from t° to 0° .

\therefore every unit of heat is indicated by $\frac{n}{mt}$ divisions

\therefore 1 division represents $\frac{mt}{n}$ thermal units

In order to use the instrument, water to about the level of fg is introduced, and left until it gets to freezing point. The cork is adjusted so that the mercury is at e . The body whose specific heat is required is weighed, heated to a given temperature, dropped into the test-tube D, and the cork inserted. The heat is given up to the lower strata of water, whose temperature rises, but as the maximum density is at 4° , if the mass be calculated so that the temperature does not rise above 4° , then the heated water keeps at the bottom. In cooling, it melts the ice, and sends the mercury along n' divisions, say. Then, if m' be the mass, s' its specific heat, and t' the temperature, the n' divisions indicate $\frac{n'mt}{n}$ thermal units obtained by cooling the mass m' from t° to 0°

$$\therefore m's't' = \frac{n' \cdot mt}{n}$$

$$\therefore s' = \frac{n'}{n} \cdot \frac{mt}{m't'}$$

The apparatus, if once set up and kept in ice after each

experiment, can be used several times. It is only necessary at each experiment to see that the index is at e .

63. The Method of Cooling.—Accurate experiments by this method are difficult, but the principle is important. It depends upon the fact that the rate at which a body loses heat depends upon (1) its *surface*, and (2) its *temperature above surrounding substances* (§§ 169, 170).

Suppose, for example, that a globe containing water at 50° be suspended in the middle of a room whose walls are at 0° . Then, neglecting any slight difference, the rate at which the globe loses heat depends upon the difference of temperature ($50^\circ - 0^\circ$) and upon the surface of the vessel. Of course, soon the difference will be 49° , then 48° , etc., and thus the rate will change.

Suppose the water be removed, and turpentine inserted at 50° . The loss of heat would be the same, as it depends upon the differences of temperature and the surface of the vessel, and not upon the substance the vessel contains.

Note the time it takes the vessel, filled with water, to cool from 40° to 39° . Let this be n seconds. Then note the time it takes to cool from 40° to 39° when the vessel is filled with turpentine. Let this be n_1 seconds.

The quantities of heat (x and x_1) that have escaped in the two cases are proportional to the times; that is, $\frac{x}{x_1} = \frac{n}{n_1}$

The calorimeter and thermometer lose heat in both cases, and therefore their water equivalent, ω , must be known.

A mass of water, m , whose specific heat is 1, has cooled 1° and lost m units of heat; \therefore total loss = $m + \omega$

A mass of turpentine, m_1 , whose specific heat is s_1 , has cooled 1° and lost $m_1 s_1$ units of heat; \therefore total loss = $m_1 s_1 + \omega$

$$\begin{aligned}\therefore \frac{x}{x_1} &= \frac{m + \omega}{m_1 s_1 + \omega} = \frac{n}{n_1} \\ \therefore \frac{m + \omega}{n} &= \frac{m_1 s_1 + \omega}{n_1} \\ \therefore s_1 &= \frac{1}{m_1} \left\{ \frac{n_1}{n} (m + \omega) - \omega \right\}\end{aligned}$$

For any other liquid, whose specific heat is s_2 , we shall have a similar expression. Therefore specific heats are readily compared.

The details of the experiment can be carried out as follows:—

(a) The calorimeter is a thin brass vessel with a lid; a sensitive thermometer passes through a cork in the lid.

(b) The water equivalent must be determined as in § 59.

(c) The experiments answer best with liquids (if solids be used, they must be pulverized). They should nearly fill the calorimeter, and equal volumes should be used in each case.

(d) The liquids should be heated to a convenient temperature, poured into the calorimeter, and then the calorimeter placed in a bath at that temperature, to ensure that both vessel and liquid are at the same temperature. Knowing the mass of calorimeter and thermometer, a second weighing with the liquid at the end of the experiment will give the mass of the liquid.

(e) The results are conveniently recorded on squared paper, the ordinates representing times, the abscissæ temperatures. Join the points by a free curve. The first part of the curve should be disregarded; for example, if the initial temperature be 100° , a uniform condition of temperature will only be attained about 95° .

In comparing specific heats, select the times of cooling for the same range of temperature in each, say from 60° to 59° , or 40° to 39° . If one of the liquids be water, then the specific heat of the other liquid can be determined for various falls of 5° at first, then 4° , 3° , etc., as the temperature sinks; the mean specific heat can be deduced for each range, and for a final result the mean of all these values can be taken.

64. True Specific Heat.—The specific heats found have in all cases been the average specific heats between certain temperatures. There is, however, no reason why we should assume that this is the specific heat at every temperature; that, for example, the specific heat of iron at 0° = the specific heat of iron at 100° , or that the specific heat of water at 0° is the

same as the specific heat of water at any other temperature—that must be a subject for experiment.

Suppose we mark on OX (Fig. 45), at equal distances, numbers, to indicate degrees of temperature, and at each degree draw a perpendicular, representing the number of units of heat required to raise the temperature of a given substance from 0° to that degree. Thus $3P$ measures the number of units of heat required to raise the temperature from 0° to

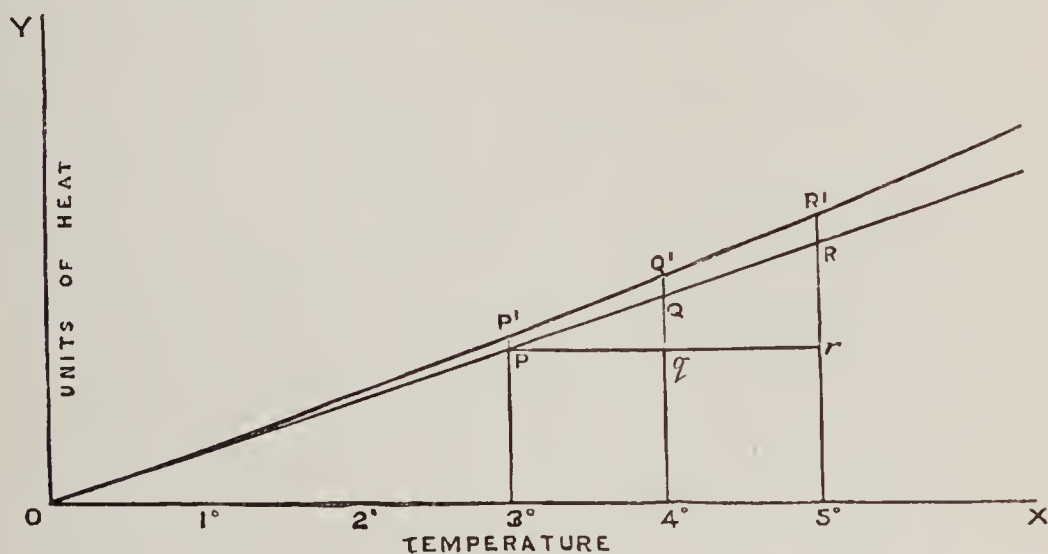


FIG. 45.

3° , $4Q$ from 0° to 4° ; then qQ = amount required to raise the temperature from 3° to 4° , rR from 3° to 5° . Joining the points, O, P, Q, R, etc., we get a curve or line. If twice $qQ = rR = \text{etc.}$, and if $3P$, $4Q$, $5R$ be some multiple of the heat required to raise the temperature from 0° to 1° , we shall have a straight line, O P Q R.

The specific heat numerically = $\frac{\text{quantity of heat}}{\text{range of temperature}}$;
i.e. the mean specific heat from 3° to 4°

$$= \frac{4Q - 3P}{4 - 3} = \frac{qQ}{1}$$

And since $2(qQ) = rR$, the specific heat is constant at all temperatures.

When experiments are carefully conducted, it is found that the true position of the points is above P, Q, R, so that a curve, O P' Q' R', is formed.

Thus to raise 1 lb. of water from 0° to 20° requires 20.01 units; from 0° to 40° , 40.05 units; from 0° to 60° , 60.14 units; from 0° to 100° , 100.5 units. From this we obtain—

		Average specific heat of water.	
Between 0° and 20°	...	1.0005	
20° „ 40°	...	1.0020	
40° „ 60°	...	1.0045	
60° „ 80°	...	1.0070	
80° „ 100°	...	1.0110	

The specific heat of water rises with the temperature (the same is true of other substances). The increase is very small, and can be disregarded in all save the most exact experiments and calculations. It is introduced to show that the specific heat of a substance, as in the case of the coefficient of dilatation, is not a constant, and cannot be exactly calculated from knowing the specific heat from 0° to 1° . The above figures, for water, are due to Regnault, who states that the specific heat of water *at any temperature* can be calculated from the formula—

$$\text{Specific heat} = 1 + 0.00004t + 0.000009t^2$$

At any temperature is used in the sense of § 33. Analogous to the construction in Fig. 31, the specific heat at any temperature will be the tangent at the point that indicates the given temperature.

The general result is that the specific heat of substances rises with the temperature.

65. High Specific Heat of Water.—Of all known substances water has the greatest specific heat. One thermal unit would raise 1 lb. of water through 1° ; but the temperature of 1 lb. of iron, with the same quantity of heat, would be raised 9° , or 9 lbs. would be raised 1° . Similarly, the same quantity of heat would raise the temperature of 30 lbs. of mercury 1° , or 4.2 lbs. of air 1° . In the case of gases it becomes more striking if we compare by volumes. The heat required to raise 1 cubic foot of water 1° would raise 4.2 times the mass of air 1° ; but as water is 770 times heavier than air,

it would therefore raise $770 \times 4.2 = 3234$ cubic feet of air 1° .

“The vast influence which the ocean must exert as a moderator of climate here suggests itself. The heat of summer is stored up in the ocean, and slowly given out during winter. This is one cause of the absence of extremes in an island climate.”

Other examples will be given in the chapter on climate.

The high specific heat of water is utilized in heating buildings by hot water, and in railway foot-warmers.

66. Specific Heat of Gases.—The specific heat of gases can be calculated—

(1) When the pressure is kept constant, the volume varying : this is the specific heat at constant pressure. Or—

(2) When the volume is kept constant and the pressure varies : this is the specific heat at constant volume.

In determining (1), the principle is to allow a mass, m , of a gas to pass through a spiral in a bath of boiling oil. It then attains the temperature t° . It then enters a specially constructed calorimeter containing a mass, m' , of water at t'° , so arranged that the gas has to pass through several spirals surrounded by the water of the calorimeter, thus giving up its heat to the water in the calorimeter, before escaping at the temperature (t''°) indicated by the water of mass m' and at atmospheric pressure ; this is the pressure the gas has been subject to throughout the experiment. Therefore—

$$ms(t - t'') = m'(t'' - t')$$

$$s = \frac{m'(t'' - t')}{m(t - t'')}$$

Elaborate precautions must be taken in order that the above conditions may be fulfilled ; particulars of the experiment will be found in Jamins' “Cours de Physique.”

The specific heat of gases at constant volume is difficult to estimate directly. It is calculated from the known relation that—

$$\frac{\text{specific heat of gases at constant pressure}}{\text{specific heat of gases at constant volume}} = \frac{C}{c} = K$$

For air, hydrogen, and many other gases a mean value of k is 1.41; for carbon dioxide it is 1.29. This will be referred to again (consult Index).

The specific heats are obtained as before by comparing with equal mass of water.

SPECIFIC HEATS OF GASES AT CONSTANT PRESSURE.

WATER = 1.

		Equal weights.		Equal volumes.
Air	...	0.2374	...	0.2374
Oxygen	...	0.2175	...	0.2405
Hydrogen	...	3.4090	...	0.2359
Nitrogen	...	0.2438	...	0.2370
Chlorine	...	0.1219	...	0.2962
Carbonic acid	...	0.2169	...	0.3307
Hydrochloric acid	...	0.1845	...	0.2333
Ammonia	...	0.5083	...	0.2966

The second column gives the units of heat required to raise equal volumes of the substances one degree, compared with the amount required to raise an equal volume of air one degree, under similar conditions of temperature and pressure, the air being compared, as in column 1, to an equal mass of water.

67. Effect of Temperature and Pressure.—The specific heats of gases, according to Regnault, do not vary with the pressure; *i.e.* the same results were obtained, whether the experiments were conducted under a pressure of 1 or 2 atmospheres, provided that the pressure was constant throughout each experiment, and in the case of air and gases not easily condensed, the specific heat is practically constant at all temperatures.

In the case of pressure, if s be the mean specific heat of a substance, δ its density, then $s\delta$ = thermal capacity of unit volume = κ .

$$\therefore \kappa \text{ (at a pressure } p) : \kappa \text{ (at a pressure } p') = s\delta : s\delta' = \delta : \delta'$$

Or, the thermal capacity of unit volume varies as the density of the gas.

The fact that the specific heat of air is unaffected by temperature and pressure points out the value of air as a thermometric substance, as equal quantities of heat will produce equal expansion on all parts of the scale, and therefore an air-thermometer will nearly agree in all parts of the scale with an absolute scale of temperature.

The variations in the specific heats of gases must be very small, or they would not have escaped a careful experimenter like Regnault. Joly,¹ however, finds that the specific heats of gases at constant volume increase with the pressure between the limits of his experiments. He has obtained the following numbers :—

Gas, and mean temperature.	Pressure in atmospheres.	Density.	Specific heat (constant volume).
Air (50° C.)	13·56 ...	0·01428 ...	0·17193
—	23·35 ...	0·02459 ...	0·17223
Carbon dioxide (55° C.)	12·10 ...	0·01979 ...	0·16922
—	21·66 ...	0·03780 ...	0·17386

68. Specific Heat changes with Change of State.—

The specific heat of water in the liquid state is unity, but that of ice is only about one-half, while the specific heat of water vapour is also about one-half.

These changes are illustrated, for some substances, in the following table :—

MEAN SPECIFIC HEATS.

	Solid.	Liquid.	Gas (constant pressure).
Water	0·504 ...	1·000 ...	0·477
Mercury	0·031 ...	0·033 ...	0·015
Lead	0·031 ...	0·040 ...	

Even when the substance remains as a solid, the specific heat varies with any change in its physical condition. For example, calcium carbonate has a specific heat of 0·2085 as aragonite, 0·2148 as chalk, and 0·2158 as marble.

¹ J. Joly, M.A., "Philosophical Transactions," 1891.

Similar changes are shown in the various allotropic forms of sulphur.

This is important in discussions relative to the mechanical equivalent of heat, and also in respect to the nature of heat. It is a subject for experiment, for example, whether the specific heat of a bar of iron is exactly equal to the same or an exactly similar bar twisted into a spiral; or whether a piece of lead, a few hours after solidifying, will have the same specific heat now as at the end of a month, when its molecules will have had time to occupy more permanent positions, or after subjecting it to great pressure in an hydraulic press. In the case of lead or steel no difference has been detected in experiments, but no assumptions must be made for these or other substances.

69. Dulong and Petit's Law.—The product of the specific heats and the atomic weights of solid substances is a constant, which is approximately 6·4; or, the specific heat of an element varies inversely as the atomic weight.

This is seen from the following table :—

				Specific heat. (a)	Atomic weight. (b)	Atomic heat. (a × b)
Aluminium	0·2143	27·4	5·9
Antimony	0·0513	122	6·3
Bismuth	0·0308	210	6·5
Copper	0·0939	63·5	6·0
Iron	0·1138	56	6·4
Platinum	0·0324	197·5	6·4
Zinc	0·0950	65·2	6·2

Another form of stating the same law is that the same quantity of heat is required to raise the temperature of an atom of all simple bodies through the same range of temperature.

Carbon, silicon, and boron for some time seemed to be marked exceptions, but the specific heats of these substances rise with the temperature. At high temperatures they approximate to the constant.

	Temperature.	Specific heat.	Atomic weight.	Atomic heat.
Carbon (diamond)	33°	0·1318	12	1·6
	247°	0·3025		3·6
	985°	0·459		5·5
Silicon (crystalline)	22°	0·1697	28	4·7
	232°	0·203		5·7

And it is probable that the law is true at very high temperatures.

If the specific heats of simple gases (equal weights) be multiplied by the relative densities (hydrogen = 1), then a product is obtained which represents the thermal capacity of equal volume. This is found to be fairly constant.

	Specific heat.	Atomic weight.	Product.
Oxygen	0·2175	16	3·48
Hydrogen	3·410	1	3·41
Nitrogen	0·2438	14	3·41

Assuming Avogadro's law, that equal volumes of gases under the same conditions as to temperature and pressure contain the same number of molecules, we conclude that the thermal capacity of all molecules of the simple gases is a constant. The molecular weight in the above gases is twice the atomic weight.

The student will remember that the specific heats of the solids, in Dulong and Petit's law, are deduced from bodies in the solid state. It is possible, when definite and direct experimental knowledge is gained of solid oxygen, hydrogen, etc., that the constant may approach 6·4.

When chemical compounds of the same class are examined, a similar law is found; thus—

	Specific heat. S.	Molecular weight. M.	Product. S × M.
Oxide of lead (PbO)	0·0509	223	11·4
Oxide of mercury (HgO)	0·0518	216	11·2
Oxide of copper (CuO) ...	0·1420	79·5	11·3

For the sulphides the product is 18.9, and for the sesquioxides the product is 27.1. The carbonates (CaCO_3 , BaCO_3) give a mean number of 21.8.

69a. Siemens's Water Pyrometer.—This is a good illustration of specific heats. The calorimeter is a copper vessel made with a double casing of copper. The space between the casings is filled with felt; this is placed inside another copper vessel to prevent radiation. A pint of water (568 grams) is placed in the calorimeter, and a thermometer, graduated in the ordinary way, is inserted. A brass scale is movable along the thermometer scale, and is graduated with 50 divisions to one degree of the thermometer scale. The zero of the sliding scale is fixed at the temperature indicated by the thermometer.

A copper cylinder weighing 137 grams (if of iron, it weighs 112 grams, and, if platinum, 402.6 grams) is placed in the furnace, and left for a few minutes until it attains the temperature of the furnace; it is then quickly dropped into the pyrometer, and the rise in temperature is read off on the sliding scale, which gives fifty times the rise in temperature in degrees.

This rise, as shown on the sliding scale, added to the temperature of the water at the commencement of the experiment, gives the temperature of the furnace.

The weight of the cylinder is selected so that its thermal capacity for one degree is equal to one-fiftieth that of a pint of water + the water equivalent of the calorimeter. In this calorimeter the water equivalent is 82 grams; that is, water + calorimeter are equivalent to 650 grams of water. The thermal capacity of the copper should be one-fiftieth of this; that is, equivalent to 13 grams of water. Therefore the weight of the cylinder should be $13 \div 0.095 = 137$ grams. As the cylinder loses weight with use, correction, of course, must be applied; for example, when its weight is only 130 grams, its thermal capacity is 12.35 thermal units; that is, a rise of one degree in the temperature of the water indicates an excess of $650 \div 12.35 = 52.6^\circ$ in the temperature of the furnace.

(This particular pyrometer is described in Baird and Tatlock's catalogue.)

WORKED EXAMPLES.

1. 20 grams of iron at 98° C. (specific heat, 0.119) are immersed in 80 grams of water at 10° C. contained in a copper vessel whose mass is 15 grams: find the resulting temperature, the specific heat of copper being 0.095 .

Let θ be the resulting temperature.

(1) The iron gives up $20 \times 0.119(98 - \theta)$ thermal units

(2) The water receives $80(\theta - 10)$ „ (a)

The calorimeter „ $15 \times 0.095(\theta - 10)$ „ (b)

$$(a + b) = (\theta - 10)(80 + 1.425)$$

Heat given up in (1) = heat absorbed in (2)

$$\therefore 2.38(98 - \theta) = 81.425(\theta - 10)$$

$$\therefore \theta(81.425 + 2.38) = 98 \times 2.38 + 814.25$$

$$= 1047.49$$

$$\therefore \theta = \frac{1047.49}{83.805} = 12.5^{\circ} \text{ C.}$$

2. Determine the specific heat of zinc (Day's Examples).

(1) Calorimeter of brass weighs 55.14 grams

(2) Calorimeter + water „ 517.50 „

(3) Zinc in pieces „ 293.65 „

It is placed in a brass cage weighing 8.48 „

(4) Thermometer: the glass weighed 1.27 „

„ mercury „ 7.62 „

Specific heats given: brass = 0.094 ; mercury = 0.033 ; glass = 0.198 .

Zinc in cage was immersed at a temperature of 99.11° C.; the water was initially at 0° C., its final temperature 5.22° C.

The calorimeter contains 462.39 grams.

The water equivalent of calorimeter and thermometer = ω

$$= (55.14 \times 0.094) + (7.62 \times 0.033) + (1.27 \times 0.198)$$

$$= 5.1832 + 0.2515 + 0.2515$$

$$= 5.686$$

Let s be the specific heat of zinc.

(1) Then zinc and cage lose $(293.65s + 8.48 \times 0.094)(99.11 - 5.22)$ thr. un.

(2) The calorimeter gains $5.22(462.39 + 5.686)$ thermal units.

$$293.65s = \frac{5.22 \times 468.076}{93.89} - 0.797$$

$$s = \frac{26.023 - 0.797}{293.65} = \frac{25.226}{293.65}$$

$$= 0.086$$

EXAMPLES. V.

1. A ball of copper at 98° C. is put into a copper vessel containing 2 lbs. of water at 15° , and the temperature of the water, ball, and vessel

after the experiment is 21°C. ; the weight of the vessel is 1 lb.; and the specific heat of copper 0.095: find the weight of the copper ball.

2. A copper ball weighing 6 lbs., taken out of a furnace and plunged into 20 lbs. of water at 10°C. , heated the water to 25° : find the temperature of the furnace. (Specific heat as above.)

3. A mass of 700 grams of copper at 98°C. , put into 800 grams of water at 15° contained in a copper vessel weighing 200 grams, raises the temperature of the water to 21°C. : find the specific heat of copper.

4. A mass of 200 grams of copper, whose specific heat is 0.095, is heated to 100°C. , and placed in 100 grams of alcohol at 8°C. contained in a copper calorimeter, whose mass is 25 grams, and the temperature rises to 28.5°C. : find the specific heat of alcohol. (London Inter. B.Sc.)

5. A glass bulb with a uniform fine stem weighs 10 grams when empty, 117.3 grams when the bulb only is full of mercury, and 119.7 grams when a length of 10.4 cm. of the stem is also filled with mercury: calculate the relative coefficient of expansion for temperature of a liquid which, when placed in the same bulb, expands through a length of from 10.4 to 12.9 cm. of the stem when warmed from 0°C. to 28°C. The density of mercury is 13.6 grams per c.cm. (London Inter. B.Sc.)

6. The specific heat of mercury is said to be $\frac{1}{30}$: what does this mean?

If the heat yielded by 1 kilogram of water in cooling down from 100° to 0°C. were employed in heating 10 kilograms of mercury initially at 20° , to what temperature would the mercury be raised? (London Matric.)

7. Describe Bunsen's calorimeter. If 100 c.cm. of water in freezing become 109 c.cm. of ice, and the introduction of 20 grams of mercury at 100°C. into a Bunsen calorimeter causes the end of the column to move through 74 mm. in a tube 1 square mm. in section, find the specific heat of mercury. (The heat required to melt 1 gram of ice is 80 units.) (London Matric.)

8. 200 grams of water at 99°C. are mixed with 200 c.cm. of milk of density 1.03 at 15°C. contained in a copper vessel of thermal capacity equal to that of 8 grams of water, and the temperature of the mixture is 57°C. : if all the heat lost by the water is gained by the milk and the copper, what is the specific heat of milk?

9. What is meant by the specific heat of water at 20°C. ?

10. Describe Lavoisier and Laplace's calorimeter. What are its defects? In an experiment, 10 lbs. of a metal are inserted at 215°C. , and $2\frac{1}{3}$ lbs. of water run from the apparatus: determine the specific heat of the metal.

11. What is Dulong and Petit's law? What explanation can you give of the case of the diamond? It is found that the specific heat of a new metal is 0.073: how could you approximately estimate the atomic weight?

12. Find the amounts of heat required to raise 1 cubic metre of dry air and of dry hydrogen at normal pressure from 0° to 100°C.

CHAPTER VI.

CHANGE OF STATE—THE NATURE OF HEAT.

70. General.—The change in molecular state can be illustrated from the forms of water. If pieces of ice weighing 1 lb. be placed in a beaker in which is inserted a thermometer, and the beaker be plunged into a mixture of ice and salt, the thermometer will soon indicate a temperature below zero. Let us suppose that it indicates -6°C .

(1) Remove the beaker and let it stand in the room. Stir the ice during the process in order to keep it at the same temperature throughout its mass. Heat is absorbed from the room, and the temperature rises steadily to 0°C . If the mean specific heat of ice be 0.504 between -6° and 0° , then $0.504 \times 6 = 3.024$ thermal units are absorbed.

(2) The ice begins to melt, and the temperature remains at 0° until the whole is changed into liquid water. The mass has continued to absorb heat, but the heat has not affected the temperature; it has been used in changing the pound of ice at 0° to water at 0° . We may state for the present that this will take 80 thermal units, the unit being the heat required to raise 1 lb. of water through 1°C .

(3) As soon as the melting is completed, the temperature again begins to rise until it reaches that of the temperature of the room. Place the beaker now over a flame. The increase in temperature continues until the thermometer indicates 100°C . In this stage the water has absorbed 100 units of heat, if we take 1 as the mean specific heat of water.

(4) The liquid changes into water vapour, and during the

process the temperature remains steady until the whole has been changed. The absorption of heat has gone on, and, as will be seen, 537 units have been absorbed. The volume at 100° under normal pressure is 1624 times the volume of 1 lb. of water at 100° .

(5) If the vapour, by any arrangement, were kept in a closed vessel, the temperature would again rise. If 0.48 be the mean specific heat of water vapour, and 200° C. the final temperature, it would absorb $0.48(200 - 100) = 48$ thermal units.

Further changes would ultimately take place if the temperature were high enough. The water would disassociate into oxygen and hydrogen. This effect we shall not discuss.

If the process be reversed, we should have—

(5) The cooling of the vapour from 200° to 100° , and 48 units of heat would be liberated.

(4) The changing of vapour at 100° into water at 100° , and the liberation of 537 units of heat

(3) The cooling of water from 100° to 0° , and the liberation of 100 units.

(2) The changing of water at 0° into ice at 0° , and the liberation of 80 units.

(1) The cooling of ice at 0° to ice at -6° , and the liberation of 3.024 units of heat.

Similar illustrations could be obtained from other substances, although, with the means at our command, all the stages could not be completely illustrated from each substance. Thus iron would only show (1), (2), and part of (3); alcohol, (2), (3), (4), and (5); oxygen, (3), (4), and (5).

Attending more particularly to the stages (2) and (4), called respectively those of fusion and vaporization—or, when the processes are performed in the reverse way, solidification and liquefaction—we have to observe that, if the experiments be repeated with pure water under normal atmospheric pressure, the temperature of fusion (or melting point) and the temperature of solidification is always at 0° C., and that the temperature of vaporization (boiling point), or the temperature of liquefaction under similar conditions, is always at 100° C.; and further, that the number of units of heat necessary to complete the

process of fusion (or the number of units of heat liberated in solidification) is constant, and, for the present, may be taken as 80 units; also that the number of units of heat necessary to completely effect the vaporization (or the number liberated during liquefaction) is constant, and may be taken as equal to 537.

71. The Nature of Heat.—Caloric.—Heat has been spoken of as entering a body and raising its temperature; of leaving it and lowering its temperature; and certain effects of expansion, of rise of temperature, and of change of state from solid to liquid, from liquid to gas, have been observed. The early idea was that heat was an imponderable fluid called caloric, which entered a body and raised its temperature, and which, on leaving it, lowered the temperature; or entering the body during change of state—as in melting ice at 0° C. to water at 0° C.—the heat became “latent,” this latent heat becoming evident to the senses when the water changed into ice. Water at 0° was, according to this theory, ice at $0^{\circ} +$ a certain amount of caloric.

Heat obtained by friction was explained by stating that, in rubbing, part of the caloric was squeezed out of the bodies.

Some of the supporters of the theory even experimented with a view to discover the change in weight when caloric entered or left a substance, and came to the conclusion that the admission of caloric made a substance lighter. The differences were shown, however, to be due to experimental errors. Lavoisier showed conclusively that a flask of water hermetically sealed showed no change of weight when the water was frozen. He further enclosed six grains of phosphorus in a strong flask, ignited it by the sun’s rays, and proved that, after combustion, there was no change in weight. This did not, however, disprove the idea of an imponderable fluid, and the entrance of this fluid into the spaces between the particles of a substance gave an apparently satisfactory view of increase in bulk in expansion, fusion, and vaporization.

72. Rumford’s and Davy’s Experiments.—Rumford, in observing the boring of cannon, noticed the enormous amount of heat generated, and performed a series of experi-

ments to determine from whence the caloric was derived. He first examined the case according to the then theory; that is, he collected the fine borings and chips, heated them to the boiling point of water, placed them in a simple calorimeter, and noted the rise in temperature. He repeated the experiment with slices of equal mass cut from the solid metal, and obtained the same rise in temperature. He concluded that the heat generated in boring was not, therefore, due to any latent heat squeezed out of the metal. To satisfy one hypothesis of the caloric theory, the capacity for heat of the borings should have been less than the capacity for heat of the solid metal. His reasoning was not quite conclusive, as the change in the state of the filings and borings, compared with the molecular condition of the solid slices, might have affected the result. Later examination showed, however, that this did not do so. (See end of § 68.)

In another experiment he arranged so that the borer and block of metal were surrounded with water. He fixed a cylinder of brass, partly bored, in a box containing 18 lbs. of water. The borer revolved 32 times in a minute, and was moved by machinery. The initial temperature was 60° F.; in an hour it was 107° F.; and in 2½ hours it boiled. He estimated the heat produced as being equal to nine wax candles each three quarters of an inch in diameter, burning the same length of time.

The source of heat could not be from change of capacity, as shown above; it could not come from the air, as this was excluded from the apparatus; nor from the water, since it underwent no chemical change; nor from surrounding objects, seeing that they took heat from the metal. He says—

“The result of this experiment was very striking, and the pleasure it afforded amply repaid me for all the trouble I had taken in contriving and arranging the complicated machinery used in making it. The cylinder had been in motion but a short time when I perceived, by putting my hand into the water and touching the outside of the cylinder, that heat was generated.”

Rumford's conclusion was, “In reasoning on this subject

we must not forget that most remarkable circumstance, that the source of the heat generated by friction in these experiments appeared to be inexhaustible. It is hardly necessary to add that that which any isolated body or system of bodies can continue to furnish without limitation, cannot possibly be a material substance; and it appears to me extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being executed and communicated in these experiments except motion."

Rumford's reasoning amounts to this—

(1) The calorists say that heat is an imponderable substance.

(2) They have an additional hypothesis, namely, that the capacity of a body for heat depends upon the quantity of heat it already contains.

(3) The experiments show that the capacities for heat of the borings and the solid are equal.

(4) Therefore the theory of caloric is untrue.

But the logical conclusion is that the hypothesis in (2) is untrue, and therefore, as Sir William Thomson points out, if calorists gave up this hypothesis, Rumford's experiments had not disproved that heat is an imponderable substance.

Rumford should have reduced both the solid iron and the borings to the same molecular condition. He might, for example, have melted both, and compared the quantity of heat necessary to melt each; or he might have dissolved them in hydrochloric acid, and obtained a solution of iron chloride, and compared the amount of heat generated in each process; the differences by either method would have been inappreciable. He then could have fairly concluded that there was nothing in the condition of the metal in the two states to account for the quantity of heat generated during the abrasion of the metals, and that, therefore, heat was not a material substance.

Rumford made a determination of the amount of work required to raise 1 lb. of water through 1°. The work, he said, could be done by one horse in a given time, and the results do not greatly differ from later determinations.

Boyle had proved that heat was produced by rubbing metals *in vacuo*. Sir Humphry Davy performed an experiment to test the caloric theory, and believed that he disproved it.

He rubbed together two pieces of ice until they melted, taking precautions to prevent heat from any source entering the ice. The friction was performed by clockwork *in vacuo*, and the complete apparatus was surrounded by melting ice. Sufficient heat was produced by friction to melt the ice. Davy then reasoned in this way: If heat be an imponderable fluid, caloric, then, in the above experiment, seeing that caloric cannot be obtained from surrounding bodies or from the air, but has been squeezed out of the ice, the water formed should have a less capacity for heat than the ice from which it was formed. But the capacity for heat of water is well known to be greater than that of ice, and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction, consequently, does not diminish the capacity of bodies for heat. The heat needed to melt the ice, then, can only be the result of friction. (Compare Rumford's reasoning.)

"The immediate cause of the phenomenon of heat, then, is motion; and the laws of its communication are precisely the same as the laws of the communication of motion."

The ordinary experiments that when a body is rubbed—a button on a piece of wood—it becomes warm, or when heat is generated by hammering, as, for example, when we raise the temperature of a piece of lead by a series of blows,—can, it should be observed, be readily explained by the caloric theory.

Speaking of experiments such as Davy's, Dr. Young puts the case against the caloric theory—

"If the heat is neither received from the surrounding bodies, which it cannot be without a depression of their temperature; nor derived from the quantity already accumulated in the bodies themselves, which it could not be even if their capacities were diminished in any imaginable degree;—there is no alternative but to allow that heat must be actually generated by friction; and if it is generated out of nothing it cannot be matter, nor even an immaterial or semi-material substance."

The examination of the relation between heat and work was continued, among others, by Mayer and Joule.

73. Heat and Work.—The experiments of Rumford and Davy were bringing into prominence the fact, not only that work produced heat, but that the heat produced was the result of the work alone, and that the heat might be measured in terms of work.

Simple experiments upon solids and liquids have been mentioned. The fire-syringe experiment (Fig. 46) illustrates it in the case of gases. The piston works lightly in the glass barrel. A piece of cotton wool is moistened with carbon disulphide, and placed in a small hole in the base of the piston. On pressing the piston quickly down, the heat produced by the compression of the air is sufficient to ignite the cotton wool.

In a later chapter the converse of this experiment will be seen.

Another experiment, due to Tyndall, is shown in Fig. 47. A brass tube is fitted

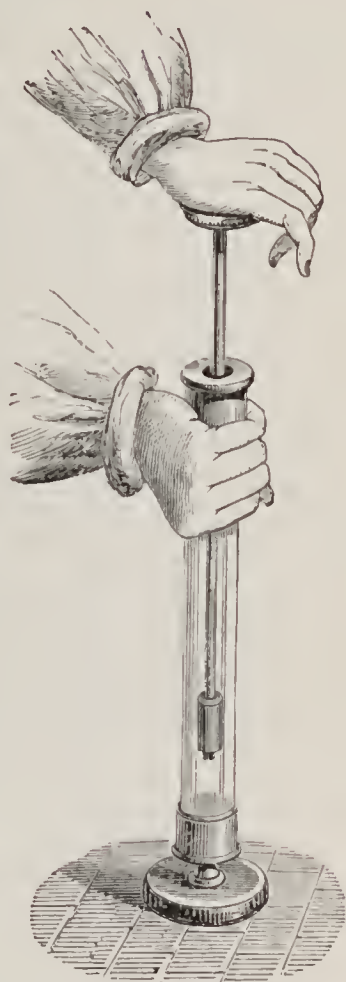


FIG. 46

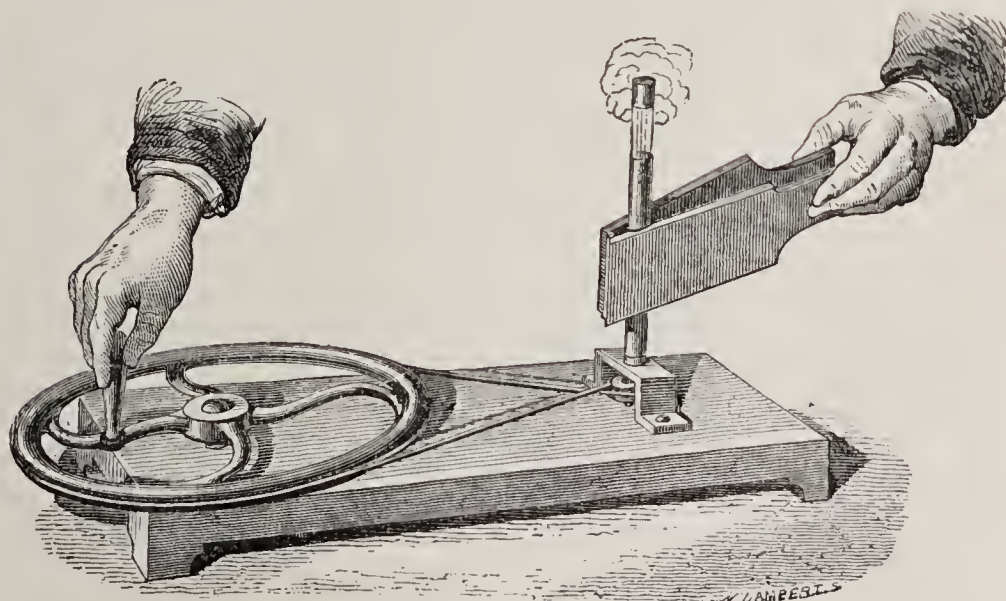


FIG. 47.

to the stand, and made to revolve rapidly by turning the wheel. It is clasped tightly between the presser lined with leather. Soon the friction causes the ether to boil and the cork is expelled.

If a piece of lead be hammered for a few seconds, a distinct rise of temperature will be detected, either by testing it with the differential thermometer or, more markedly, with the thermo-pile.

74. Note on Dynamical Units.—Every quantity is expressed by a phrase that consists of two parts: (1) the numerical portion, and (2) the unit of the quantity; for example, the distance 14 yards can be expressed as 14 y (unit 1 yard), 7 fathoms (unit 1 fathom), 42 feet (unit 1 foot), etc.

Dynamical quantities can all be derived from units of length, mass, and time; these are called fundamental units.

The standard of *length* in England is 1 yard; that of France, 1 metre. Both standards are preserved with care, and copies have to be made at definite temperatures (§ 22). The usual practical and scientific units used are sub-multiples of these: 1 foot and 1 cm.

1 metre = 39.37 inches; and therefore 1 foot = 30.48 cm.

The symbol for length is *s* (space).

The English standard of *mass* (*m*) is 1 lb.; the French standard is 1 kilogram. Each is a piece of platinum preserved in the respective countries. The French scientific unit is 1 gram.

1 lb. = 0.45359 kilogram = 453.59 grams

The general unit of *time* (*t*) is 1 second.

The system of units derived from the centimetre, the gram, and the second is called the centimetre-gram-second system, written C.G.S. system. The English adopt a foot-pound-second system; and a system could be built on any selected units of length, mass, and time.

From the units of length, mass, and time are derived the units of—

Area: 1 square foot ; 1 square cm.

Volume: 1 cubic foot ; 1 c.cm.

Other units, such as 1 square inch, 1 square metre, are in use ; but we are dealing more particularly with those needed for our purpose.

1 c.cm. of water at 4° C. weighs 1 gram

1 litre = 1000 c.cm.

1 cubic foot of water weighs 1000 ozs. nearly

1 gallon = 277.276 cubic inches

1 gallon of water weighs 10 lbs. nearly

Speed (v) is the rate at which a body moves with respect to surrounding objects. Sometimes the term "velocity" is used instead of "speed." In speed motion alone is considered ; velocity implies the further consideration of direction.

Speed, if uniform, is measured by the number of units of length (feet or cm.) passed over in unit time (1 second).

The units of speed are: (1) English, 1 foot per second ; (2) C.G.S., 1 cm. per second.

1 foot per second = 30.48 cm. per second

Acceleration (a) is the rate at which a body changes its speed ; for example, at one instant the speed of a body is 40 feet per second, a minute later it is 56 feet per second, a minute later 72 feet per second. If the increase has been uniform, the speed has changed at the rate of 16 feet per second in every minute. Time is repeated twice, and it is usual to keep the second as unit in each case.

The units of acceleration are: (1) English, 1 foot per second per second ; (2) C.G.S., 1 cm. per second per second.

1 foot per second per second = 30.48 cm. per second per second

If we attempt to move a body at rest we are conscious of muscular effort, whether we succeed in starting it in motion or not. There is a similar muscular effort exerted when we attempt to stop or retard the motion of a moving body. In both cases we exert *force*.

Newton's first law of motion states—

That every body continues in a state of rest or of uniform

motion in a straight line except in so far as it is compelled to alter that state by some *force*.

Momentum is the product of mass and velocity (mv). The units of momentum are: (1) the momentum of a mass of 1 lb. moving with a velocity of 1 foot per second; and (2) the momentum of a mass of 1 gram moving with a velocity of 1 cm. per second.

Newton's second law is—

Change of momentum is proportional to the force acting upon a body, and takes place in the direction in which the force acts. The change can, of course, only be effected in a certain time.

A mass of 6 lbs. moves with a speed of 8 feet per second; a second later its speed is 3 feet per second.

$$\text{Momentum at beginning of second} = 6 \times 8 = 48$$

$$\text{,, ,, end ,, ,,} = 6 \times 3 = 18$$

\therefore force acting for 1 second against the body is proportional to 30

$$\text{Or force} \times \text{time} = ft = m(v' - v'')$$

The change in velocity, if uniform, divided by the time, is the acceleration; or it is the acceleration at the particular time, if we make the time small enough.

$$\therefore f = m \frac{v' - v''}{t} = ma$$

The unit of force is that force which, acting on unit mass for unit time, produces unit change of momentum.

(1) English: that force which, acting on the mass of 1 lb., changes its velocity 1 foot per second in every second. This unit is called the *poundal*.

(2) The C.G.S. unit, called the *dyne*, is that force which, acting on the mass of 1 gram, produces a change of velocity of 1 cm. per second in every second.

In the above example the force is 30 poundals.

1 pndl. actg. on 1 lb. prod. chng. of vel. of 1 ft. per sec. in ev. sec.

$$\therefore 1 \quad ,, \quad 453.59 \text{ gr.} \quad ,, \quad ,, \quad 30.48 \text{ cm.} \quad ,, \quad ,,$$

$$\therefore 1 \quad ,, \quad 1 \text{ gr.} \quad ,, \quad ,, \quad 453.59 \times 30.48 \text{ cm.} \quad ,, \quad ,,$$

$$\therefore 1 \quad ,, \quad 1 \text{ gr.} \quad ,, \quad ,, \quad 13,825.4 \text{ cm.} \quad ,, \quad ,,$$

$$\therefore 1 \text{ poundal} = 13,825.4 \text{ dynes}$$

1 lb. has been used as the unit of mass ; it is sometimes taken as a unit of weight. Either idea may be retained if we are careful to keep to the same name throughout. When we take 1 lb. as unit of mass, we consider merely the quantity of matter it contains—a quantity that can be used for manufacturing or other purposes. As unit of weight, we are considering its push downwards, or the pull it exerts on a spring-balance, for example ; that is, we consider it as a force. That it is best to consider it as a unit of mass will be seen from the following applications.

If the standard pound be suspended from a very delicate spring-balance that indicates a pull of 1 lb. on the scale in London, then, if we move to the equator, it will register less than 1 lb. ; that is, the force downwards, due to gravitation, has decreased. Nearer to the pole it will indicate more than 1 lb. The pull downwards, then, is not constant, although there has been no change in the mass ; 1 lb. of iron will make into the same number of the same kind of nails in any of the three places.

If the 1 lb. be allowed to fall from rest at Greenwich, its velocity, as shown by experiment, at the end of the first second will be 32·2 feet per second.

$$\begin{aligned} \text{Momentum at starting} &= 1 \times 0 = 0 \\ \text{,, gained in 1 second} &= 1 \times 32\cdot2 = 32\cdot2 \text{ units} \end{aligned}$$

The force acting upon it, due to gravity, is the weight of 1 lb. This force, acting on 1 unit of mass, produces a change of 32·2 units of momentum per second in 1 second ; that is, the weight of 1 lb. at Greenwich = 32·2 poundals. At Paris the velocity at the end of the first second would be 32·18 feet per second.

$$\therefore \text{the weight of 1 lb. at Paris} = 32\cdot18 \text{ poundals}$$

Similarly, the weight of 1 lb. at the equator = 32·09 poundals.
The weight of 1 lb. is called the force of 1 lb.

The differences in the values of the weight of 1 lb. are small. Between London and Paris it is less than $\frac{1}{4000}$ of the force at either place, and can be neglected in engineering and

practical operations. 1 lb. considered as a force is commonly used by practical men because it is a more suitable unit than 1 poundal, which is roughly equal to 1 lb. force $\div 32$ = the weight of $\frac{1}{2}$ oz., and is therefore inconveniently small.

If we take g to express the acceleration due to gravity, which varies with the latitude and distance above the sea-level, then always—

$$1 \text{ lb. weight} = g \text{ poundals}$$

$$1 \text{ gram weight} = g \text{ (in centimetres) dynes}$$

The acceleration due to gravity, in centimetres per second, is 978.1 at the equator, 980.94 at Paris, 981.17 at Greenwich, and 981.34 at Manchester.

A force does *work* (w) when it moves its point of application. The measure of the work is the product of the force and the distance moved in the direction in which the force acts.

$$w = fs$$

(1) The English unit is the foot-poundal; it is the work done by 1 poundal in moving through 1 foot.

(2) The C.G.S. unit, the erg, is the work done by 1 dyne in moving over 1 cm.

$$\begin{aligned} 1 \text{ foot-poundal} &= 13,825 \text{ dynes working through } 30.48 \text{ cm. (1 foot)} \\ &= 13,825 \times 30.48 \text{ dynes cm.} \\ &= 421,394 \text{ ergs} \\ &= 4.214 \times 10^5 \text{ ergs nearly} \end{aligned}$$

The common units, based on the weight of 1 lb., 1 gram, 1 kilogram, etc., are—

(1) English: work done by a force of 1 lb. working through 1 foot, called a foot-pound.

$$\begin{aligned} 1 \text{ foot-pound} &= g \text{ foot-poundals} = 32.2 \times 4.214 \times 10^5 \text{ ergs} \\ &= 1.36 \times 10^7 \text{ ergs nearly (at Greenwich)} \end{aligned}$$

$$\begin{aligned} (2) \text{ French: } 1 \text{ gram-centimetre} &= g \text{ ergs} = 981 \text{ ergs nearly} \\ 1 \text{ kilogram-metre} &= (1000 \times 100) \text{ gram-cm.} \\ &= g \times 10^5 \text{ ergs} = 9.81 \times 10^7 \text{ ergs} \end{aligned}$$

The poundal and foot-poundal, the dyne and the erg, are in all cases independent of g , and are called absolute units.

The foot-pound, the kilogram-metre, etc., involve ultimately the value of g , and are called gravitation units.

Energy is the capacity for doing work, and is measured in the same units as work.

If a mass of 10 lbs. be raised 6 feet from the ground, 60 foot-pounds of work are done. The mass, by virtue of its position in relation to the earth, can in falling do 60 foot-pounds of work. It can raise, with suitable machinery, 10 lbs. through 6 feet, or 20 lbs. through 3 feet, neglecting friction. The catapult, when stretched, can do work: it can project, let us say, a stone weighing 1 oz. to a height of 50 feet, and therefore can do $50 \div 16 = 3\frac{1}{8}$ foot-pounds, or nearly 100 foot-pounds, of work. Its capacity for work depends upon the relative positions of the particles of the indiarubber. The work that can be done by a bent spring, by a head of water, are other examples of capacity for work, due to the positions of the relative parts of a system. This is called *potential energy*. Its measure is force into effective distance.

A body has also a capacity for work due to its motion. The work done by a cannon-ball, the work done (destructive) by ships in collision, the work done by the moving hammer, are examples. Energy due to motion is called *kinetic energy*.

Kinetic energy is measured in absolute units by the product of half the mass into the *square* of the velocity.

A mass of 5 lbs. is moving with a velocity of 10 feet per second.

$$\text{Kinetic energy in foot-pounds} = \frac{1 \times 5 \times 10^2}{2} = 250 \text{ foot-}$$

$$\text{pounds} = \frac{250}{32} = 7\frac{13}{16} \text{ foot-pounds (if } g = 32)$$

This is the work the body can do before it is brought to rest.

A mass of 2 lbs., 64 feet from the ground, possesses potential energy. It can, by virtue of its position relative to the earth, do 128 foot-pounds, or 128*g* foot-pounds, of work. If the body falls freely, at the end of 1 second it will have fallen approximately 16 feet, and will have a velocity of 32 feet per second.

$$(a) \text{ Potential energy} = 2 \times 48 = 96 \text{ foot-pounds}$$

$$(b) \text{ Kinetic energy} = \frac{2 \times 32 \times 32}{2 \times g} = 32 \text{ foot-pounds}$$

$$\text{Total energy} = a + b = 128 \text{ foot-pounds}$$

Just before it touches the ground its velocity is 64 feet per second.

$$\text{Potential energy} = 0$$

$$\text{Kinetic energy} = \frac{2 \times 64 \times 64}{2 \times g} \text{ foot-pounds} = 128 \text{ foot-pounds}$$

The total energy of a system, unless it acts upon or is acted upon by another system, is a fixed quantity.

When the mass strikes the ground, the energy is not apparently as easy to trace. A thud is heard, there is the rebounding of the mass and of particles of earth, but soon all are at rest, and energy seems destroyed; for the energy needed to start the sound-wave (particles of air must be set in motion) is small compared with 128 foot-pounds. A wave will have been transmitted through the earth; this will take up some of the energy; these waves die away, but a certain amount of heat is produced. The increase in temperature is very small, and soon there is a cooling down, and uniformity of temperature ensues. The mass after impact would be found to be heated; it again soon cools down to the surrounding temperature; the energy has disappeared, and heat seems to be the total result.

The following sections will show that, by doing work, heat may be generated, and further, that the amount of heat generated is always proportional to the work done; also that, by the action of heat, work can be done, and the work done is proportional to the amount of heat that disappears. This has led to the idea that heat is a form of energy. It has already been stated that, in a hot body, the particles are vibrating; we may therefore consider sensible heat as kinetic energy.

In the illustration with the falling body, if the total heat-energy could be estimated when all was apparently at rest, it would equal 128 foot-pounds.

From consideration of the various forms of energy, the doctrine of the conservation of energy has been stated; it has been found to answer every possible test, and is one of the most important generalizations in science.

“The total energy of any body or system of bodies is a quantity which can neither be increased nor diminished by any mutual action of these bodies, though it may be transformed into any of the forms of which energy is susceptible.”

75. Change of Units.—Dimensions.—Some examples have already been given. As the original memoirs relating to heat are in varying units, it will be well to consider the general principles.

A speed, by definition, will always be represented by a length, **L**, divided by a time, **T**. A speed of 28 feet per second = $28 \frac{\text{feet}}{\text{second}}$; if we wish to change this into cm. per minute, we only need deal with the $\left(\frac{\text{foot}}{\text{second}}\right)$ unit, and then multiply by the numerical portion.

$$1 \text{ foot} = 30.48 \text{ cm.}; 1 \text{ second} = \frac{1}{60} \text{ minute.}$$

$$\therefore 1 \text{ foot per second} = \frac{\text{foot}}{\text{second}} = \frac{30.48 \text{ cm.}}{\frac{1}{60} \text{ minute}} = 1826.8 \text{ cm. per minute} = 1826.8 \frac{\text{cm.}}{\text{minute}}$$

\therefore to change the numerical value of a speed in feet per second into cm. per minute, multiply by 1826.8

$$V = \frac{L}{T}$$

is called the dimensional equation of a speed. Length is involved to the first power in the numerator; time, to the first power in the denominator. It is sometimes written—

$$V = LT^{-1}$$

Acceleration is a velocity \div time.

$$\therefore A = \frac{V}{T} = \frac{L}{T} \div T = \frac{L}{T^2}; \text{ or } A = LT^{-2}$$

An acceleration of 100 miles per minute per minute = $100 \times \frac{\text{mile}}{\text{minute} \times \text{minute}}$ (units : 1 mile, 1 minute). To change these to feet per second per second, we have length involved to the first power ; time, inversely as the second power.

$$\therefore \frac{\text{mile}}{\text{minute} \times \text{minute}} = \frac{\mathbf{L}}{\mathbf{T}^2} = \frac{5280}{60 \times 60} \times \frac{\text{foot}}{\text{second} \times \text{second}}$$

$$= \frac{44}{30} \times \frac{\text{foot}}{\text{second} \times \text{second}}$$

$$\therefore 100 \text{ miles per minute per minute}$$

$$= \frac{44}{30} \times 100 \text{ feet per second per second}$$

$$= 146\cdot\dot{6} \text{ feet per second per second}$$

We can, with a greater expenditure of work, obtain the result as follows :—

$$100 \text{ miles per minute per minute}$$

$$= 100 \times 5280 \text{ feet per minute per minute}$$

$$= \frac{100 \times 5280}{60} \text{ feet ,, second ,, minute}$$

$$= \frac{100 \times 5280}{60 \times 60} \text{ feet ,, second ,, second}$$

$$\text{Area} = \mathbf{L}^2$$

$$\text{Volume} = \mathbf{L}^3$$

$$\text{Momentum } (\mu) = \text{mass} \times \text{velocity} = \mathbf{M} \cdot \frac{\mathbf{L}}{\mathbf{T}} = \frac{\mathbf{ML}}{\mathbf{T}}$$

$$\text{Force } (\mathbf{F}) = \frac{\mu}{\mathbf{T}} = \frac{\mathbf{ML}}{\mathbf{T}^2}$$

$$\text{Or } \mathbf{F} = \text{mass} \times \text{acceleration} = \mathbf{MA} = \frac{\mathbf{ML}}{\mathbf{T}^2}$$

Poundal units are 1 lb., 1 foot, 1 second.

Dyne ,, ,, 1 gram, 1 cm., 1 second.

\therefore to change poundals into dynes (1 lb. = 453·59 grams ; 1 foot = 30·48 cm. ; time is unchanged), multiply by

$$\frac{453\cdot59 \times 30\cdot48}{1 \times 1} = 13,825$$

To change poundals into a unit of force measured in yards,

$$\text{tons, and minutes, the multiplier is } \frac{\frac{1}{2240} \times \frac{1}{3}}{\frac{1}{60} \times \frac{1}{60}} = \frac{30}{56}$$

$$\text{A pressure is a force per unit area} = \frac{\mathbf{F}}{\mathbf{L}^2} = \frac{\mathbf{M}}{\mathbf{LT}^2}$$

$$\text{Density is mass per unit volume} = \frac{\mathbf{M}}{\text{volume}} = \frac{\mathbf{M}}{\mathbf{L}^3}$$

$$\text{Work} = \text{force} \times \text{distance} = \mathbf{FL} = \frac{\mathbf{ML}^2}{\mathbf{T}^2}$$

$$\therefore 1 \text{ foot-poundal} = \frac{453.59 \times (30.48)^2}{1 \times 1} \text{ ergs} = 4.214 \times 10^5 \text{ ergs}$$

$$1 \text{ foot-pound} = g \text{ foot-poundals} = g \times 4.214 \times 10^5 \\ = 1.36 \times 10^7 \text{ ergs (if } g = 32.2)$$

$$1 \text{ gram-cm.} = g \text{ ergs} = 981 \text{ ergs (if } g = 981 \text{ cm.)}$$

$$\therefore 1 \text{ foot-pound} = \frac{1.36 \times 10^7}{981} = 13,825 \text{ gram-cm.}$$

Or direct—

$$\text{Work} = \mathbf{F} \times \mathbf{L}$$

$$\therefore 1 \text{ foot-pound} = 453.59 \times 30.48 = 13,825 \text{ gram-cm.}$$

$$(a) \text{ Kinetic energy} = \frac{1}{2}mv^2. \quad (b) \text{ Potential energy} = \mathbf{F} \times \mathbf{L}.$$

\therefore dimensions of energy are—

$$(a) = \mathbf{M}(v^2) = \frac{\mathbf{ML}^2}{\mathbf{T}^2}$$

$$(b) = \mathbf{F} \times \mathbf{L} = \frac{\mathbf{ML}^2}{\mathbf{T}^2}$$

i.e. in both cases the same dimensions as work.

Power is the rate at which a body works

$$= \frac{\mathbf{W}}{\mathbf{T}} = \frac{\mathbf{ML}^2}{\mathbf{T}^3}$$

$$1 \text{ horse-power} = 33,000 \text{ foot-pounds per minute} = 550 \text{ foot-pounds per second}$$

$$= 550 \times 32.2 \text{ foot-poundals per second}$$

$$\begin{aligned}
 &= \frac{550 \times 32.2 \times 453.59 \times (30.48)^2}{1^3} \\
 &= 7.5 \times 10^9 \text{ ergs per second} \\
 &= \frac{7.5 \times 10^9}{981} \text{ gram-cm. per second} \\
 &= 7.6 \times 10^6 \text{ gram-cm. per second} \\
 &= 76 \text{ kilogram-metres per second}
 \end{aligned}$$

In heat we have a special unit to introduce ; we must have some unit to express a degree of temperature on any scale : let this be Δ .

The thermal unit is the heat required to raise unit mass of a substance through 1° .

$$\therefore \text{dimensions of thermal unit} = \mathbf{M}\Delta$$

The unit is sometimes defined as the quantity required to raise unit volume through one degree of its temperature ; its dimensions will therefore be $\mathbf{L}^3\Delta$ when so defined.

The coefficient of expansion = $\frac{\text{change of length, area, or volume}}{\text{original length, area, or volume}}$ per degree ; the fractional part is a ratio, and therefore has no dimensions ; therefore in dimensions—

$$\text{Coefficient of expansion} = \frac{1}{\Delta}$$

Specific heat is a ratio merely, and has no dimensions.

Thermal capacity of unit volume is specific heat \times density ; therefore its dimensions are those of density = $\frac{\mathbf{M}}{\mathbf{L}^3}$

It will be shown in the next section that the unit of heat = $\mathbf{J} \times$ units of work.

\mathbf{J} , called Joule's equivalent, is the mechanical equivalent of unit heat.

\mathbf{J} is the number of units of work per unit of heat.

\therefore for its dimensions we have $\frac{\mathbf{ML}^2}{\mathbf{T}^2} \div \mathbf{M}\Delta = \frac{\mathbf{L}^2}{\Delta\mathbf{T}^2}$ (work in absolute units)

$$\text{Or } \mathbf{ML} \div \mathbf{M}\Delta = \frac{\mathbf{L}}{\Delta} \text{ (work in gravitation units)}$$

i.e., in changing the value of J from one system of units to another system, the unit of mass is never involved.

76. Joule's Experiments.—One of Joule's methods was practically that followed by Rumford (Fig. 48).

A copper vessel, B, was provided with a brass paddle-wheel (indicated by the dotted lines), which rotated about a vertical

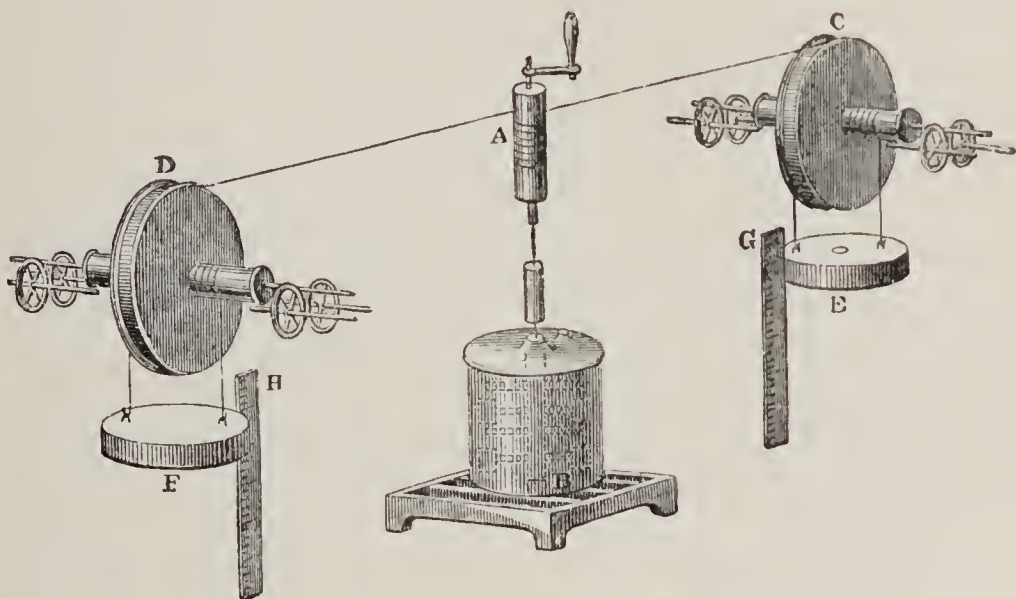


FIG. 48.

axis, A. The axis was rotated by the weights E and F, the cord for each weight being so arranged that, falling, each weight rotated the axis in the same direction. Each weight could fall in the experiment 63 feet, the distance being measured on the scales G and H.

The paddles, churning the water, raised its temperature; when the weights had fallen to the bottom, by loosing a pin (not shown in the figure) A was disconnected from the paddles, and by turning the handle at the top of A, the weights were raised, the pin inserted, and the weights again allowed to fall.

The axes of the pulleys (D, C) were rested in friction-wheels, to diminish the friction as far as possible. Small corrections were made for loss of heat, the heating of the calorimeter and paddle, radiation, etc.

If m = the weight of the two weights, h the distance fallen

in one descent, and v the velocity with which they reach the bottom, then, during each fall the work done, in foot-pounds

$$= w = mh - \frac{1}{2} \frac{m}{g} v^2$$

mh = potential energy = total energy at the beginning
 $\frac{1}{2}mv^2 \div g$ = kinetic energy = total energy at the end

$\therefore w$ = loss of energy = work done by the paddles

If the weights fall n times, the total work done, in foot-pounds, is $nw = W$.

Weight of water in calorimeter \times degrees through which the temperature had risen = thermal units given to the water (H).

The experiment was repeated in various forms with the greatest care to eliminate errors, using other liquids, such as mercury, to show that the result was independent of the material; so that we can accept the numbers obtained as being almost free from error; the general result being that the ratio $\frac{W}{H}$ in all experiments equals a constant, $J = 772$ foot-pounds when degrees Fahrenheit are used.

From a large number of similar experiments Dr. Joule concluded that to raise 1 lb. of water 1° Fahrenheit requires the expenditure of 772 foot-pounds of work. If the thermometer be marked in Centigrade degrees, the expenditure of work will be 1389.6 foot-pounds.

772 foot-pounds of work is the mechanical equivalent of one thermal unit in the Fahrenheit scale when 1 lb. is the unit of weight and 1 foot the unit of length.

If the measurements were only needed for general purposes, no appreciable error would be made by using this number; but as the measure of the work done varies with the force due to gravity, and this varies with the latitude and the distance above the sea-level, the following particulars should be added: The experiment was performed at Manchester, and the thermal unit was the heat needed to raise 1 lb. of water from 50° to 51° F.

This is a result obtained from experiment, and does not

give us any definite clue to the nature of heat; nor is any hypothesis as to the nature of heat involved. What the experiments really show is that—

Whenever a certain amount of energy is converted into heat, the number of units of heat is always proportional to the energy.

This is called the *First Law of Thermo-dynamics*, and is expressed as follows:—

“When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence, or are generated.”

The value of J in feet and $C.^{\circ}$ is $772 \times \frac{9}{5} = 1390$ foot-pounds

$$1 \text{ lb.} = 0.4536 \text{ kilog.}; 1 \text{ foot} = 0.3048 \text{ metre}$$

$$\begin{aligned} 1 \text{ th. unit (kilog., } C.^{\circ}) &= 1390 \div 0.4536 \text{ foot-pounds} \\ &= 1390 \div 0.4536 \times 0.3048 \text{ metre-pounds} \\ &= 1390 \div 0.4536 \times 0.3048 \times 0.4536 \text{ m.-kgs.} \\ &= 424 \text{ kilogram-metres of work} \end{aligned}$$

$\therefore J = 424$ when the units are 1 kilogram, 1 metre, $1^{\circ} C$.

We deduce this at once by units (see end of § 75).

$$J = \frac{L}{\Delta T}$$

$$\begin{aligned} \therefore 772 \frac{\text{foot}}{F.^{\circ}} &= 772 \frac{\text{foot}}{\frac{5}{9} C.^{\circ}} = 1390 \frac{\text{foot}}{C.^{\circ}} = 1390 \frac{0.3048 \text{ metre}}{C.^{\circ}} \\ &= 424 \frac{\text{metre}}{C.^{\circ}} = 42,400 \frac{\text{cm.}}{C.^{\circ}} \end{aligned}$$

In Absolute Units.—1 unit of heat = 772 g foot-pounds
= 772×32.2 foot-pounds = 24,858 foot-pounds (if $g = 32.2$).

Now, the dimensions of J are $\frac{L^2}{\Delta T^2}$

$$\begin{aligned} \therefore 24,858 (\text{foot, lb., second, system}) &= 24,858 \cdot \frac{(30.48)^2}{\frac{5}{9} \cdot 1^2} = 4.157 \\ &\times 10^7 (\text{C.G.S. system}) \end{aligned}$$

The work of Rowland makes 772 too low for the value of J ; 777 is probably nearer the true result. He also obtained

numbers which indicate that J is not constant ; he found the minimum value at 29° C. (774.5). The value 772 (4.16×10^7 in C.G.S.) is, however, retained throughout this work.

77. Molecular Theory of Heat.—According to modern views, all substances are supposed to be made up of molecules, a molecule being the smallest possible portion of the substance that can exist by itself as that substance. These molecules are so small that they are far beyond recognition by the most powerful microscope. Each molecule may consist of one, two, or more atoms.

The molecules are ever in motion. They are highly elastic, so that, if compressed vibrations like those of a sounding bell or tuning-fork take place, there may also be movements among the component parts of the molecules. The molecules may, in addition, be rotating, and may also be moving as a whole along a certain path ; the form and extent of the motion depend upon the particular condition of the substance. If the substance be a solid, then the molecules are more or less restrained in their movements ; they never move far from certain definite centres. They whirl round these centres like planets in their orbits, but never lose their connection with the adjacent molecules unless subjected to some great shock. Solids thus resist any change of form.

In liquids the molecules can move from place to place freely, slip easily over each other, so that the form of a liquid readily changes. The cohesion between the molecules in liquids is, however, great, so that it is difficult to affect the volume of the liquid.

When the liquid is changed to a gas, in addition to an increase in the various forms of movement, the molecules move rapidly among each other, colliding, moving in straight lines, and impinging against the walls of the containing vessel and against each other. For an average distance that is always much greater than the diameter of the molecules, they meet with no obstruction. This is called the *free mean path* (§ 173). The effect of the radiometer is obtained by making, by exhaustion, this free mean path sufficiently great. No matter how great the space into which a portion of the gas be introduced, the molecules separate and attempt to penetrate

into every part. As long as there is an envelope they will press against it. They offer as a mass comparatively slight resistance to change of form or of volume under ordinary conditions, and if subjected to force rapidly close up.

78. Internal and External Work.—The general effect of heat upon a body is to increase the intensity of the motion of the molecules; and it may also separate them further from each other, moving the sides of the containing vessel and overcoming resistance. Thus we may have an internal effect and an external effect.

(1) If the substance, on being heated, increases in volume, then it must push back the surrounding substances—air, for example; in so doing it does work; this is the external work. On the contrary, the air (or other substances) may press upon the substance, diminish its bulk, and thus do external work on the substance. The external work done by a rod in expanding is very small, seeing that its boundary moves a very short distance; the external work done by a gas in expanding may be considerable.

(2) The internal work, we see, may consist in an increase in the energy of the particles.

(a) The atoms of which the molecule is composed may vibrate more rapidly, and you have increase of energy of vibration; or they may change their rotation, and then there is change of energy of rotation; both being forms of kinetic energy. This is called intramolecular work.

(b) The molecules may have increased kinetic energy imparted to them by increasing their average velocity.

(c) The molecules may have been separated against the force of cohesion, causing change of volume, change of state. They are in a condition such that they will tend to come together again, and in so doing will do work; so that we have heat-energy changed into potential energy.

(d) The heat may be so great that the molecules may break up, as the molecules of water will break up into molecules of oxygen and hydrogen.

Change in the temperature of a body is due to (b) and (a), the change in the total kinetic energy of the molecules. In

the past experiments it is that part of the heat we have spoken of as sensible heat. This is only part of the internal work. In the other part of the internal work (*c*) the energy no longer exists as heat. (*c*) may be partially illustrated by pulling apart two balls joined by indiarubber; work has been done upon the two balls, and exists as the potential energy of the balls; by virtue of their position they can again do work. It represents the so-called latent heat.

Heat-energy communicated to a body = (*a*) energy of internal work (includes increase of temperature) + (*b*) energy of external work + (*c*) energy communicated to external bodies by radiation + (*d*) kinetic energy communicated to external bodies. Generally it is so arranged that (*c*) and (*d*) are each so small that they can be neglected.

Let us consider a few examples. (1) Take the case of a mass of iron receiving heat-energy. We have—

Internal work. An increase in temperature, or increase in the kinetic energy of the molecules.

In expanding, work is done against molecular forces.

External work. The iron expands, and pushes the surrounding air, and does external work. This is so small it can generally be neglected. If the iron were *in vacuo*, so that it received no opposition to its efforts to expand, the amount would be *nil*.

(2) Heat-energy is supplied to a cubic foot of ice at 0° C. We have work done among the molecules in fusion, so that the ice can exist as water. These molecules, in returning to the original condition, will give up the same amount of energy. This is the so-called latent heat of ice, and we see that it is not heat at all, but energy existing as potential energy. The cubic foot of ice occupies about eleven-twelfths cubic foot as water; so that external work has been done upon that substance by the pressure of the atmosphere. This can be readily calculated. Imagine the change to have taken place on one face. The pressure of the atmosphere is (15×144) lbs. per square foot nearly. The face moves one-twelfth foot; therefore the work done by the atmosphere is—

$$15 \times 144 \times \frac{1}{12} = 180 \text{ foot-pounds of work}$$

To effect this change the ice has received about 80×62.5 thermal units = 5000 thermal units, equivalent to (5000×1390) foot-pounds (Centigrade scale) of work; or 6,950,000 foot-pounds of work. In comparison with this the 180 foot-pounds of external work done upon the substance is negligible.

(3) Consider the case of a cubic foot of water at 100° C. receiving heat until it vaporizes into steam at 100° under ordinary atmospheric pressure. There is first the internal work done in changing the liquid into a gas; that is, work done among the molecules in vaporization. To change 1 lb. of water takes 537 thermal units. 1 cubic foot weighs about 62.5 lbs. Therefore the energy spent in the change is $537 \times 62.5 \times 1390$ in foot-pounds, following the Centigrade scale; that is, 46,651,875 foot-pounds of work.

A cubic foot of water becomes about 1700 cubic feet of steam. If we suppose the water enclosed in a cylinder with rigid sides and base, 1 foot, we see that it will lift a piston placed in the water 1700 feet, and do $1700 \times 144 \times 15$ foot-pounds of work; that is, 3,672,000 foot-pounds of work, taking the pressure of the atmosphere as 15 lbs. on the square inch. Thus we have—

Total work ...	46,651,875	foot-pounds
External work	3,672,000	„
Internal work	42,979,875	„

The internal work is more than eleven times the external work.

79. Melting Point.—Let us now return to fusion, and examine first the melting points of solids. For substances whose melting point is low it can be determined by melting them (wax, paraffin) and drawing them into very thin capillary tubes. Cut off a piece of the tubing when the substance has set, and attach it by an indiarubber band to a thermometer (Fig. 49). Place the whole in a liquid which boils at a higher tempera-

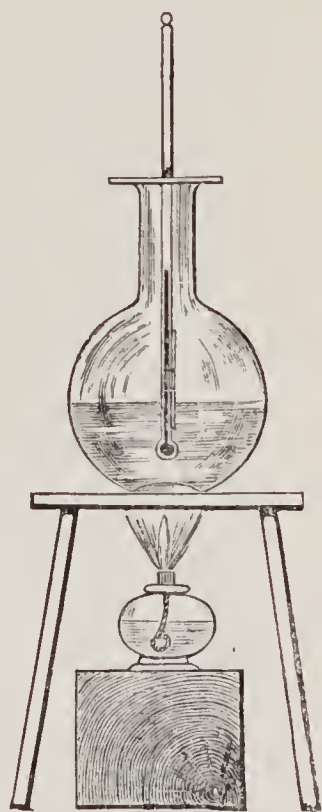


FIG. 49.

ture than the melting point. Heat slowly, and observe (1) the temperature at which fusion begins, t . Remove the flame, and observe (2) when solidification begins, t' . $\frac{t + t'}{2}$ will be the melting point.

From such experiments the laws of fusion have been deduced.

80. Laws of Fusion.—(1) Every solid substance begins to melt at a certain definite temperature, if the pressure remains constant. This is called the melting point (or, in the reverse process, the freezing point).

(2) If the mass be kept stirred so as to ensure uniformity of temperature, the temperature remains constant from the beginning to the ending of the fusion.

MELTING POINTS (C.°) AT A PRESSURE OF 1 ATMOSPHERE.

Mercury	... -40°	Sulphur	.. 115°
Ice	... 0°	Bismuth	... 260°
Butter	... 33°	Lead	... 327°
Phosphorus	... 44°	Iron	... 1600°
White wax	... 65°	Platinum	... 1775°

81. Latent Heat of Fusion.—The number of units of heat required to change a unit of mass of a solid at its melting point into a liquid at the same temperature is called the latent heat of fusion of the solid.

In melting the ice at 0° C. to water at 0° C. (§ 70) the heat absorbed had no effect upon the temperature. For this reason it was said to be latent, and was called by Black the latent heat of water. The heat thus become latent was supposed to be stored away in the substance as heat, and became evident as sensible heat when the liquid passed into the solid state. We have seen that the heat is engaged in doing internal work, in overcoming the cohesion of the molecules so that the solid ice can exist as liquid water; that until the change of state is completed there will be no rise of temperature; and that latent heat is potential energy.

Water = ice + potential energy.

There is also generally a change in volume. If the substance, in liquefying, increase in volume, then the energy as heat necessary to produce fusion equals the potential energy of the molecules (latent heat) together with the external work done in overcoming the pressure of the atmosphere, this latter being a small quantity comparable with the former (§ 78). If the volume is less in the liquid state, external work is done on the substance.

82. Black's Methods.—Two of Black's methods possess an historical interest. Two similar thin flasks, one containing 5 ozs. of melting ice at 32° F., the other 5 ozs. of water at 33° F., were suspended in a room whose temperature (47° F.) remained constant during the experiment.

(1) In $\frac{1}{2}$ hour the temperature of the water rose to 40° F., the ice-flask still indicating 32° .

(2) In $10\frac{1}{2}$ hours the ice was melted, and the temperature of the flask had risen to 40° F.

The ice-flask had received in $10\frac{1}{2}$ hours twenty-one times as much heat as the water-flask received in $\frac{1}{2}$ hour; the latter received 7 units of heat during that time. Therefore to melt 5 ozs. of ice at 32° F. to water at 32° F., and raise its temperature to 40° , requires 147 units; that is, the latent heat of water is 139 units (the unit of mass is 5 ozs.). This rough result, on the Centigrade scale, will be $139 \times \frac{5}{9} = 77$.

His second method was a simple one of mixing ice with water, and from the resulting temperature determining the latent heat.

He took a piece of ice weighing $59\frac{1}{2}$ drachms, and placed it in $67\frac{1}{2}$ drachms of water at 190° F. In a few seconds the ice was melted, and the final temperature was 53° F. He previously determined that the water equivalent of the glass vessel was 4 drachms.

$\therefore 67\frac{1}{2} + 4 = 71\frac{1}{2}$ drachms of water fell in temperature from 190° to 53° , *i.e.* through 137° , and gave up $71\frac{1}{2} \times 137 = 9795\frac{1}{2}$ heat-units (taking 1 drachm as the unit of mass)

(a) $59\frac{1}{2}$ drachms of ice at 32° F. were melted to water at

the same temperature; and (b) $59\frac{1}{2}$ drachms of water were raised through 21° , *i.e.* from 32° to 53° .

$$(b) \text{ required } 59\frac{1}{2} \times 21 = 1249\frac{1}{2} \text{ heat-units}$$

$$\therefore (a) \text{ required } 9795\frac{1}{2} - 1249\frac{1}{2} = 8546 \text{ heat-units}$$

$$\therefore \text{ to melt 1 drachm of ice requires } 8546 \div 59\frac{1}{2} = 144 \text{ heat-units}$$

\therefore the latent heat of fusion, using the Fahrenheit scale, is 144

\therefore „ „ „ Centigrade „ 80

a number that more accurate experiments have not changed.

To simplify the calculation, we may conduct the experiments so that the final temperature is the freezing point.

For example, leaving out the water equivalent of the vessel—
1 lb. of ice or snow at 32° F., mixed with 1 lb. of water at 176° F., gives 2 lbs. of water at 32° .

\therefore at once the latent heat of fusion = 144 (Fahrenheit scale)

Or 1 lb. of ice at 0° C., mixed with 1 lb. of water at 80° C., gives 2 lbs. of water at 0° .

\therefore the latent heat of fusion is 80 (Centigrade scale)

83. Laboratory Method.—This is simply Black's method with corrections. The calorimeter already described, provided with a lid and a stirrer, can be used.

Let m be the mass of water at temperature t (the experiment should be so arranged that the temperature at the beginning of the experiment is as much above the temperature of the room as it is below it at the end of the experiment); and ω , the water equivalent of the calorimeter, thermometer, etc.; M , the mass of dry ice added in pieces. The mass M is obtained by weighing the calorimeter before the ice is added and at the end of the experiment. Let θ be the final temperature.

The water has lost $(m + \omega)(t - \theta)$ units of heat. These units of heat have melted M units of ice, and have raised the temperature θ° .

If x be the latent heat of water, these operations require $Mx + M\theta$ units of heat.

$$\therefore Mx + M\theta = (m + \omega)(t - \theta)$$

$$\therefore x = \frac{(m + \omega)(t - \theta)}{M} - \theta$$

A calorimeter weighs 18 grams; after adding water, the weight is 168 grams, the temperature (t) being 24.5°C .; some dry ice at 0° is added; after the whole is melted, the lowest temperature reached is (θ) 13.5°C .; the total weight is now 186 grams: find the latent heat of ice, given that the water equivalent (ω) of calorimeter, thermometer, etc., is 3 grams.

The mass of water (m) is $168 - 18 = 150$ grams

„ „ ice (M) is $186 - 168 = 18$ „

(a) The calorimeter and contents lose $(150 + 3)(24.5 - 13.5)$
 $= 153 \times 11$ heat-units $= 1683$ heat-units

$$[(m + \omega)(t - \theta)]$$

(b) 1683 heat-units melt 18 grams of ice, and raise the temperature of water formed from 0° to 13.5° ; the latter takes $18 \times 13.5 = 243$ heat-units $[Mx + M\theta]$

\therefore to melt 18 grams requires $1683 - 243 = 1440$ heat-units

\therefore to melt 1 gram „ „ $1440 \div 18 = 80$ „

\therefore the latent heat of ice $= 80$

A slight modification of the method enables us to calculate the latent heat of fusion of solids that are solid at the ordinary temperature. Let us take, for example, the case of sulphur.

The following particulars will be required. They must either be taken from the results of other experiments or must be determined:—

(1) The melting point of sulphur, $t = 115^\circ \text{C}$.

(2) The specific heat of solid sulphur, $c = 0.203$.

(3) „ „ liquid „ „ $c' = 0.234$.

(4) The mass of water in the calorimeter (m) and the water equivalent (ω). Let the sum of these two ($m + \omega$) in an experiment $= 12$ grams, the initial temperature, t_1 , being 16°C .

The sulphur is melted, heated to t'° (say 150°), and poured

into the calorimeter. After mixing, the final temperature, θ (in the experiment, 27°), is read. The increase in weight of the calorimeter and contents gives M , the mass of sulphur (4 grams).

Let the latent heat of fusion for sulphur be L .

A. The sulphur gives up heat in three stages—

(a) Cooling from 150° to 115° ; heat-units liberated = $4(150 - 115) \times 0.234 = 32.76$. $[M(t' - t)c]$

(b) Solidifying from liquid at 115° to solid at 115° ; heat-units liberated = $4L$. $[ML]$

(c) Cooling in the solid state from 115° to 27° ; heat-units liberated = $4(115 - 27) \times 0.203 = 61.32$. $[M(t - \theta)c']$

A total of $32.76 + 4L + 61.32$ heat-units = $4L + 94.08$.

$$[M(t' - t)c + ML + M(t - \theta)c']$$

B. The water and calorimeter receive $12(27 - 16)$ heat-units = 132 . $[(m + \omega)(\theta - t_1)]$

\therefore assuming that all the heat from the sulphur is given to the calorimeter and water—

$$4L + 94.08 = 132$$

$$\therefore L = 9.5$$

Or generally—

$$M(t' - t)c + ML + M(t - \theta)c' = (m + \omega)(\theta - t_1) \quad (\text{i.})$$

where L is the only unknown term. The specific heat of solids (c) is known in most cases, or it can be readily determined. c' , the specific heat of liquids, is more difficult to determine. If, however, we repeat the above experiment, beginning at another temperature, t'' , and ending at a final temperature θ' , M' being the mass of sulphur, then—

$$M'(t'' - t)c + M'L + M'(t - \theta')c' = (m + \omega)(\theta' - t) \quad (\text{ii.})$$

we have two equations (i.) and (ii.), and two unknowns, L and c' .

\therefore both of these can be determined

Substances heated to high temperatures lose heat rapidly by radiation. In attempting to determine the latent heat of fusion of tin, for example (melting point 237°C.), the substance must be heated to a temperature about 250° . Corrections

must, therefore, be introduced to allow for the loss in transferring it to the water, and allowance must also be made for the loss due to the cooling of the calorimeter.

A substance like paraffin, that is solid at ordinary temperatures, and which melts below 100°C ., may be added to the calorimeter in the solid state, the water being at a temperature, t_1 , above the melting point, t . Let the final temperature be θ , the temperature of the solid paraffin t' . Then, using letters as in the above equations—

$$(m + w)(t_1 - \theta) = M(t - t')c + ML + M(\theta - t)c'$$

LATENT HEATS OF FUSION.

Ice	80	Tin	14.6
Nitrate of soda	63	Bismuth	12.6
Zinc	28	Sulphur	9.4
Platinum	27	Phosphorus	5.0
Silver	25	Mercury	2.8

84. Solution.—Heat has been used to fuse solids. They also pass into the liquid state when placed in a suitable liquid, as salt in water. Heat, again, is necessary; this is taken from the heat of the whole mass, and the temperature falls.

Place the two bulbs of the differential thermometer in dishes of water at the same temperature. When the index is stationary, add crystals of a soluble substance (sodium sulphate) to one dish; as it dissolves, the index will show that the temperature of the solution is falling. This is the principle of many freezing mixtures. Mixtures of solids, or of solids and liquids, provided that one dissolves, cause a lowering of temperature

The following are some examples of such mixtures, the first temperature being that of the substance before mixing:—

Ice and salt	down to	-22°C .
Sodium sulphate (8 parts), hydrochloric acid (5 parts)	from 10° ,,	-17°C .
Sodium phosphate (9 parts), dilute nitric acid (4 parts)	,, 10° ,,	-29°C .
Calcium chloride (4 parts), snow (3 parts)	,, 0° ,,	-51°C .

In the above mixtures, the solid substance used is solid at ordinary temperatures. Much lower temperatures have been obtained by using as the solid a substance that is a gas at ordinary temperatures, but which has, by pressure or reduction of the temperature, been changed into the solid state. This will be illustrated when we speak of the liquefaction of gases (§ 118).

The lowering of temperature may be disguised by chemical action taking place between the substances. For example, if phosphorus pentoxide be placed in water, it dissolves, and there is a distinct rise in temperature—the heat-units, the result of chemical action between the substance and water, being greatly in excess of the heat-units needed to dissolve the substance; dissolving sodium hydrate or potassic hydrate in water gives a similar result. This part of the subject belongs, however, rather to chemistry than to physics.

85. Saturation.—On adding carefully a solid to a liquid that will dissolve it, a point is reached at any temperature when no more will dissolve: the liquid is saturated at that temperature. Generally, on raising the temperature more solid dissolves; this, however, offers many exceptions. Common salt, for example, seems equally soluble in water at all temperatures.

86. Solidification.—If a liquid pass into the solid state, the thermal units necessary to change the solid into the liquid state are liberated. The potential energy is changed into heat. The freezing point is the same temperature as the melting point under the same pressure, and until solidification is completed the temperature remains constant.

Under certain conditions, the liquid may be cooled below the freezing point without solidification taking place.

Water, for example, deprived of air and placed in a clean capillary tube has been cooled down to -20° C. without freezing. In ordinary vessels, if they be not agitated, water will remain liquid below 0° C., but on shaking or dropping into it a piece of ice, solidification takes place. In all cases, as soon as solidification begins, the temperature rises to the freezing point.

The phenomenon is readily illustrated by making a strong solution of sodium sulphate, evaporating it until a few drops on cooling crystallize. If the solution be poured into a clean glass flask, a thermometer inserted, a piece of cotton wool be placed in the neck, and the flask be placed so that it is not disturbed, the solution will cool down to the temperature of the room without solidifying. If a crystal of sodium sulphate be dropped into it, the mass crystallizes, and the temperature, as shown by the thermometer, rises.

Sodium hyposulphite, whose crystals melt readily in their own water of crystallization on placing the vessel containing them in hot water, is also suitable for the experiment.

If the substance be dissolved in a suitable solvent, the solid is formed on cooling the mixture sufficiently. The effect of the presence of the substance is to reduce the freezing point of the liquid. For example, if salt be dissolved in water, the mixture remains liquid at temperatures below 0° C. A familiar illustration occurs in the liquid formed by adding salt to the snow on the tram-lines in winter: the snow dissolves, but a liquid mixture of water and salt is formed, much colder than the snow.

Blagden, in 1788, stated that the lowering of the freezing point was proportional to the amount of salt dissolved. This is known as *Blagden's law*, and is practically true for weak solutions.

Raoult has shown, further, that this law is applicable to most solutions, provided the mass of salt be not more than $\frac{1}{100}$ of the mass of the liquid. The researches of Raoult suggest that some simple general law may be deduced for solutions.

87. Guthrie's Researches.—Cryohydrates.—If we reduce the temperature of a weak mixture of water and salt (to take a special example), then, at a temperature below zero depending upon the proportion of salt, solidification of part of the pure water takes place, and therefore a stronger solution of brine is left. This fact was known to the earlier experimenters.

Guthrie, experimenting upon strong solutions, has shown that at first crystals are deposited that have a definite composition,

and contain two molecules of water to one of salt ($\text{NaCl}, 2\text{H}_2\text{O}$); if these crystals be removed, and the temperature be further lowered, the whole mass freezes at about -21°C. , and the solid has a definite composition of twenty-one molecules of water to two of salt ($2\text{NaCl}, 21\text{H}_2\text{O}$). To these compounds he gave the name *cryohydrates*.

The cryohydrates are definite compounds that possess a definite melting point and crystallize in definite forms.

The cryohydrate represents the mixture that will the longest resist solidification. In the case of water and salt, the lowest possible temperature to which a given mixture can keep solid is -22°C. , and this is possible when a mixture is made represented by $2\text{NaCl}, 21\text{H}_2\text{O}$.

88. Change of Volume.—Change of state is in general accompanied by change of volume. The greater number of solids expand when liquefied, and therefore the solid sinks in the liquid; examples are gold, lead, paraffin, wax. Cast iron, ice, bismuth, antimony, contract on liquefying; the solid, therefore, floats on the liquid. Castings taken from the former lack the sharpness of those taken from the latter set of solids. Gold coins are therefore stamped.

Substance.				Melting point. C.	Density of solid.	Density of liquid.
Bismuth	260°	9.82	10.05
Lead	327°	11.4	10.4
Iron	1600°	6.95	6.88
Water	0°	0.9167	1.0

The case of water is important in nature. 11 cubic feet of water at 0° become roughly 12 cubic feet of ice at 0° . Therefore the ice formed on ponds floats on the surface and retards further freezing; otherwise the lakes and ponds and rivers would become a mass of solid ice, that in many cases the sun of summer would be unable to melt.

(a) In the case of ice, cast iron, etc., we have heat-energy = internal work — external work done on the solid in contracting.

(*b*) In the case of gold, paraffin, etc., heat-energy = internal work + external work done in expanding.

This would suggest that increase or decrease of pressure in these two classes would lead to different results.

In class (*a*) increase of pressure lowers the melting point. In class (*b*) increase of pressure raises the melting point (see § 91 and chapter xii.).

It was predicted by Professor T. Thomson, and confirmed by experiment by Sir W. Thomson, that increase of pressure lowers the melting point of ice. The melting point is lowered 0.0075° C. per atmosphere. In the case of paraffin, on the other hand, which ordinarily melts at 46.3° C., it melts at 49.9° C. when subject to a pressure of 100 atmospheres.

89. Ice.—The work done by ice in expanding against the atmosphere is not observable, but if it be enclosed in strong cases, as in water-pipes, we have burst pipes due to expansion, the flaws being made evident during the thaw.

The force due to this expansion is strikingly shown in the experiments of Major Williams in Canada. Bombs were filled with water, closed, and exposed to the frost. On freezing, the plugs were forced out and the bombs split; a cylinder of ice issued from the opening wherever made (Fig. 50).

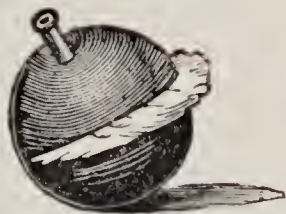


FIG. 50.

The lowering of the temperature would cause the water to expand in attempting to pass into ice, this would increase the pressure, and probably lower the melting point, so that in bursting a stream of water issued. The pressure being relieved, and the temperature being below the temperature at which water freezes under ordinary pressure, the water at once froze.

90. Regelation.—Faraday drew attention to the fact that, when two pieces of ice are pressed together, they freeze together at the place of contact. Bottomley suspended a block of ice upon two supports, passed a wire round the block, and attached a weight to it; the wire gradually cut its way through, the block freezing as the wire passed. The explanation is that the increased pressure lowers the melting point, and part melts. The water occupies less volume, the pressure

is thus relieved, the water readily escapes from the place, and the pressure on it being relieved, and it being below freezing point, it again freezes.

This is seen on a large scale in the motion of glaciers. In the slow yet river-like motion there will be enormous pressure down the mass. At particular points—the concave side of a bend, for example—the pressure will be enormously increased. The general temperature, save at the surface, will not be much below 0° , as there is a continuous trickle of water. The melting point will be lowered, and part of the ice will melt. The water takes up less volume, and there is thus a relief at once; the water flows away and is at once frozen. Thus the mass acts as if it had the power of bending, or as if its nature were viscous or plastic.

91. Melting Point of Ice lowered by Pressure.—That the melting point is lowered by pressure is well illustrated by a piece of apparatus first made by Mousson. A strong cylinder of steel is closed at one end with a screw and at the other with a screw-piston provided with a handle. On turning the handle the piston moves in the tube. The piston is inserted, the apparatus inverted and nearly filled with water, a small piece of copper placed in the water sinks until it is in contact with the piston. The whole is plunged into a freezing mixture until the water freezes. The screw is then placed on the open end, and the whole again inverted, so that we have a cylinder of ice with the piece of copper on the top of it, and the screw-piston above the piece of copper. The whole apparatus is kept at a temperature of -18° C., and the handle turned so that the piston presses upon the ice. When the pressure exerted was equal to 13,000 atmospheres, the pressure was relieved. On taking out both screw-piston and screw-stopper, it was found that the piece of copper was resting upon the screw-stopper.

The temperature was -18° C. throughout. Evidently at a pressure near 13,000 atmospheres the ice had melted, so as to allow the copper to sink from one end to the other; that is, at a pressure about 13,000 atmospheres the melting point was lowered 18 degrees Centigrade.

A laboratory experiment, due to Tyndall, can be performed with two box-wood moulds. A convenient form is that in which one contains a hemispherical cavity, while the other has a hemispherical protuberance that does not quite fill the cavity. On placing broken pieces of ice or snow in the cavity, placing the second block above, and compressing either by a Bramah press or by suitable screws, the whole can be moulded into a cup-shaped piece of ice.

Pieces of ice or snow can be made into a solid block of ice by placing them in a steel mortar, inserting a close-fitting pestle, and driving the pestle down with a hammer.

The whole question is further illustrated in making a snow-ball. If the temperature of the air be below 0° C., the snow will not join, and the boy cannot exert sufficient pressure to lower its melting point so as to produce regelation. The warmth of the hand raises its temperature nearly to melting point, and then the available pressure is sufficient.

92. Fusion of Alloys.—The melting point of an alloy is generally lower than that of the metals forming the alloy. This is especially characteristic of alloys of lead and bismuth, as will be seen from the following table :—

Parts by weight.							
Lead (326° C.) ...	1	...	1	...	1	...	2
Bismuth (267° C.) 0	...	0	...	2	...	5	
Tin (238° C.) ...	5	...	3	...	1	...	3
Melting points	194° C....	187°	...	$94^{\circ 1}$...	100°	

The low melting points of these alloys, combined with the fact that they expand on solidifying, make them suitable for casts and stereotyping; they are also used for solder.

When an alloy is gradually heated, it generally softens and becomes pasty some degrees below the point at which it liquefies. For example, an alloy of two parts of tin and two parts of lead begins to soften at 185° C., and finally liquefies at 189° C. The reverse process is observable as an alloy cools. There is first the passage from a liquid into the pasty condition; this takes some time, the temperature re-

¹ Rose's fusible metal, which melts, therefore, in hot water.

maining stationary, and latent heat being liberated. Then follows the cooling through this viscous state, and the final solidification at the lower temperature.

Rudberg studied various alloys of lead and tin, and noted how long it took them in a liquid state to cool through 10°C . Whatever proportions of the metals were used, he noticed that the rate of cooling was slowest near 187°C ., the temperature at which they finally solidified. This was the temperature at which the alloy 3 of tin to 2 of lead solidified without passing through the viscous state. He noticed a similar phenomenon in other mixtures, and concluded that an alloy might be considered as a mixture of two definite alloys, each with its own melting point; that the alloy with the lower melting point first began to melt; the tendency of the mixture to flow would depend upon the proportion of this alloy. Finally, when the higher melting point was reached, the whole liquefied. For mixtures of lead and tin, the lower melting point was always 187° , the melting point of the alloy 1 of lead to 3 of tin; this he called a chemical alloy. This definite lower melting point does not, however, seem to be as definite as Rudberg's conclusions suggest.

Mixtures of lead and tin are used as fusible plugs in boilers. Steam at each pressure has a definite temperature (§ 97). Suppose the safe pressure in a boiler must not exceed 180 lbs. on the square inch, the temperature of the steam will be 373°F . If a fusible plug made of 2 tin and 2 lead be inserted, at 365°F . the plug will soften, and at 372°F . will melt, and then the steam will blow off.

The proportions of the alloy for each temperature are determined by experiment.

Fusible plug.				Softens at			Melts at	
2	tin	2	lead	365°F	372°F .
2	,,	6	,,	372°F	383°F .
2	,,	7	,,	$377\frac{1}{2}^{\circ}\text{F}$	388°F .
2	,,	8	,,	395°F	408°F .

According to Rudberg, the number in column 2 should be 368 in all cases.

93. Viscous Solids.—Iron has not any definite melting point; it gradually softens, and in this condition can be welded, and ultimately melts. Glass passes through a similar viscous state. It may be that this is a property of many solids, although the range of temperature for which they remain viscous may be so small that it escapes detection.

WORKED EXAMPLES.

1. A pound of ice at 0° C. is thrown into 6 lbs. of water at 15° C. contained in a copper vessel weighing 3 lbs., and when the ice is melted, the temperature of the water is 2° C. : find the latent heat of fusion of ice, the specific heat of copper being 0.095. (London Matric., 1880.)

The water equivalent of the vessel is $0.095 \times 3 = 0.285$ lb.

\therefore water + calorimeter are equivalent to 6.285 lbs.

\therefore they give up to the ice $(6.285)(15 - 2) = 81.705$ thermal units

2 of these are used in raising the melted ice at 0° to 2° C.

$\therefore 81.705 - 2 = 79.705$ heat-units must be used in melting 1 lb. of ice from ice at 0° to water at 0° C.

\therefore latent heat of fusion = 79.7

2. 20 grams of ice, contained in a copper vessel weighing 20 grams, is placed in a freezing mixture whose temperature is -20° ; vessel and ice are now plunged into water contained in a calorimeter whose water equivalent is 5 grams, the temperature of the calorimeter being 60° C. ; the final temperature is required to be 10° C. : find the mass of the water. The mean specific heat of ice = 0.5.

(a) Heat required to raise tempera- }
ture of ice and copper to 0° } = $\begin{cases} 20(20 \times 0.5 + 20 \times 0.095) \\ = 20(10 + 1.9) = 238 \text{ heat-units} \end{cases}$

(b) Heat required to melt the ice to }
water at 0° } = $20 \times 80 = 1600$ heat-units

(c) Heat required to raise the water }
at 0° and copper at 0° to 10° } = $\begin{cases} 20 \times 10 + 20 \times 10 \times 0.095 \\ = 200 + 19 = 219 \text{ heat-units} \end{cases}$

\therefore total = $238 + 1600 + 219 = 2057$ heat-units

(d) Calorimeter, in cooling from 60° to 10° , supplies $5 \times 50 = 250$ heat-units

$\therefore 2057 - 250 = 1807$ heat-units must come from the water

Each gram will supply 50 heat-units.

\therefore mass of water = $\frac{1807}{50} = 36.14$ grams

3. The density of ordinary phosphorus is 1.83; it melts at 44° C., and unit volume becomes 1.043; its latent heat of fusion is 5: compare the

external work with the internal work during liquefaction. The pressure of the atmosphere = 14.7 lbs. per square inch.

Imagine 1 cubic foot of solid phosphorus just covered with water to prevent the oxidizing action of the air. Let the expansion take place on one face only.

(1) 5 units of heat are equivalent to $5 \times 1390 = 6950$ foot-pounds of work = total work.

(2) The atmosphere is pushed back through 0.034 foot.

$$\therefore \text{external work} = 144 \times 14.7 \times 0.034 = 71.97 \text{ foot-pounds}$$

$$\therefore \text{internal work} = 6950 - 71.97 = 6878.03$$

$$\therefore \frac{\text{internal work}}{\text{external work}} = \frac{71.97}{6878.03} = \frac{1}{95} \text{ approximately}$$

4. A leaden bullet weighing 2 ozs. strikes a target with a velocity of 1000 feet per second; its temperature is 16°C . : if two-thirds of the energy of the bullet be used in raising its temperature, determine the final temperature. (Specific heat of lead = 0.032; melting point, 326°C .; $g = 32$.)

$$\text{The kinetic energy} = \frac{1 \times 2 \times (1000)^2}{2 \times 16} = \frac{10^6}{16} \text{ foot-pounds}$$

$$1 \text{ thermal unit} = 1390 \text{ foot-pounds} = 1390g \text{ foot-pounds}$$

$$\therefore \text{total kinetic energy is equivalent to } \frac{10^6}{16 \times 1390 \times 32} = 1.41 \text{ thermal unit}$$

$$\therefore \frac{2}{3} \text{ of } 1.41 = 0.94 \text{ thermal unit is used in heating the bullet}$$

$$\text{To raise the temperature of bullet } 1^\circ \text{C. requires } 0.032 \times \frac{2}{16} = 0.004 \text{ th. u.}$$

$$\begin{aligned} \therefore \text{final temperature} &= 16 + 0.94 \div 0.004 \\ &= 16 + 235 = 251^\circ \text{C.} \end{aligned}$$

5. We can readily determine the velocity a bullet must have in order to fuse it. Let the mass be 1 gram. (Specific heat = 0.031.)

(1) To raise its temperature from 16° to 326°C . requires $310 \times 0.031 = 9.61$ thermal units.

(2) To fuse it requires 5.4 (latent heat of fusion of lead) thermal units.

$$\begin{aligned} 9.61 + 5.4 &= 15 \text{ thermal units are equivalent to } 15 \times 42,400 \times g \text{ ergs} \\ &= 15 \times 4.2 \times 10^7 \text{ ergs} \end{aligned}$$

If v be the velocity of the body at impact-

$$\text{The kinetic energy} = \frac{1}{2}mv^2 = \frac{1 \times v^2}{2} \text{ ergs}$$

$$\therefore v^2 = 30 \times 4.2 \times 10^7 = 12.6 \times 10^8$$

$$\begin{aligned} \therefore v &= \sqrt{12.6 \times 10^8} \text{ cm. per second} \\ &= 3.56 \times 10^4 = 35,600 \text{ cm. per second} \\ &= 356 \text{ metres per second} \end{aligned}$$

EXAMPLES. VI.

1. Can ice at 32° F., and at the ordinary atmospheric pressure, have its temperature raised still higher? If not, why not?

2. The mechanical equivalent of heat is 1390 foot-pounds Centigrade. What does this statement mean? If the standard substance were iron (whose specific heat is 0.114) instead of water, what would be the value of the mechanical equivalent of heat?

3. Find the resulting temperature (Centigrade) in the following mixtures:—

(a) 5 lbs. of snow at 0° with 20 lbs. of water at 30° .

(b) 3 lbs. of ice at -10° with 30 lbs. of water at 60° .

(c) 8 lbs. of iron at 200° with 2 lbs. of ice at 0° .

(d) 1 gram of phosphorus at 0° with 13 grams of water at 25° .

4. How many heat-units are needed to change?—

(a) 3 lbs. of ice at -5° C. into water at 10° .

(b) 4 lbs. of sulphur at 50° C. into liquid sulphur at 300° .

Express the results in units of energy.

5. The latent heat of fusion of ice is 79.5. The specific gravity is 0.917. 10 grams of metal at 100° C. are immersed in a mixture of ice and water, and the volume of the mixture is found to be reduced by 125 c.mm. without change of temperature: find the specific heat of the metal.

6. The specific heat of iron is 0.113: how many pounds of iron at 250° C. must be introduced into an ice calorimeter to produce 2 lbs. of water?

7. What do you mean by external and internal work as applied to a substance? 1 lb. of copper at 0° C. is raised to 30° C., (a) in a vacuum; (b) under ordinary atmospheric conditions; (c) when under a pressure of 100 lbs. on the square inch. Under which condition will it require most heat? Give reasons for your answer.

8. Ice melts at 32° F., and wax at 140° F. A mass of ice at 31° , and a mass of wax at 139° F., are separately compressed by suitable means. Could either of these, by a sufficient increase of pressure, be melted? Give reasons for your answer.

9. Explain the phenomena of regelation, and illustrate your explanation from glaciers and the ice formed by the wheels of vehicles passing over snow.

10. Find the number of heat-units required to change 1 lb. of ice at -10° to steam at 160° C. How would you arrange your apparatus to have steam at such a temperature?

11. 50 lbs. of iron fall freely through a height of 150 feet: if the kinetic energy be entirely converted into heat, and the heat be used in raising the temperature of the iron, find the rise in temperature.

CHAPTER VII.

CHANGE OF STATE—VAPORIZATION AND CONDENSATION.

94. Vaporization.—The change of a liquid into its vapour, and the fixity of the boiling point, have been referred to in § 70, where water was treated as a typical liquid. The process of changing a substance from the liquid state into the gaseous state is called vaporization, the reverse process being called condensation. Part of the liquid vaporizes before the boiling point is reached; the gradual disappearance of water in vessels exposed to the air, and the drying up of rain in the streets, are everyday phenomena. The change, however, goes on much more rapidly at the boiling point.

In liquids the molecules are not restricted in their path as is the case with solids. They impinge one upon the other, but the force of cohesion has been so far overcome that they slip readily over each other, and there is no average position that they occupy. The *average* velocity of the molecules of the liquid will be less than the *average* when changed into vapour, but some may have a velocity greater than that of the vapour; when such molecules come to the free surface separating the liquid and its vapour, they may break through the surface and mingle with the molecules of vapour. This is vaporization. The molecules at the same time are further separated and their potential energy is increased. Molecules of the vapour may in a similar way rush into the liquid, when we have condensation. Both actions take place probably at the same time, the excess of either determining under which phenomenon the process shall be classed; the

maximum excess of molecules evaporating over those condensing takes place at the boiling point.

To effect the change in the vibrations and the speeds of the molecules, energy is needed; the amount is measured by the internal work. All substances increase in volume when they change into vapour. If in such increase they do work, as, for example, in overcoming the pressure of the atmosphere, then energy is also needed to do external work.

When vaporization takes place at the free surface only, it is termed "evaporation." This takes place at all temperatures, and it is to evaporation that the change of the greatest amount of water into vapour is due in nature.

95. Vaporization in Vacuo.—The general study is best begun by an examination of the phenomenon of vaporization *in vacuo*.

Three tubes about 32 inches long are filled with mercury and inverted in the ordinary way, so that a Torricellian vacuum is formed in each (Fig. 51). One (A) remains during the experiment, and serves as a barometer. Small quantities of volatile liquids are forced up the other tubes by the aid of a pipette. Take the case of water (B). The small drop, when it reaches the vacuum, at once evaporates, and the level of B is depressed. The vapour exerts a pressure, measured in inches or millimetres of mercury, by the difference of the levels of A and B. As more water is allowed to rise, a further depression takes place, until under the conditions of temperature no more will evaporate, and a layer of water forms on the top of the mercury. The addition of further water does not perceptibly increase the depression (neglecting the pressure of the mass of water itself); there is thus for the particular temperature a maximum pressure of water vapour.

If, for example, the temperature of the room be $10^{\circ}\text{C}.$, the mercury in B will be 9 mm. below the level of A, that is, the maximum pressure of water vapour at 10° is equal to



FIG. 51.

the pressure of a column of mercury 9 mm. high. If the temperature be 20° , the maximum pressure is 17 mm.

Time must be allowed for the tube B to return to the temperature of the air in each experiment, because the heat-energy necessary to produce evaporation will be taken from the water and the vapour, and the temperature will fall.

If the tube be depressed in a deep trough (Fig. 52), as long as there is a space containing vapour above the mercury, the height above the mercury column remains constant (this must be done slowly, otherwise heat is generated); more water vapour condenses. If the tube be raised so that the top of B is far above A (Fig. 51), the level still remains constant as long as there is a layer of water; more water simply evaporates.

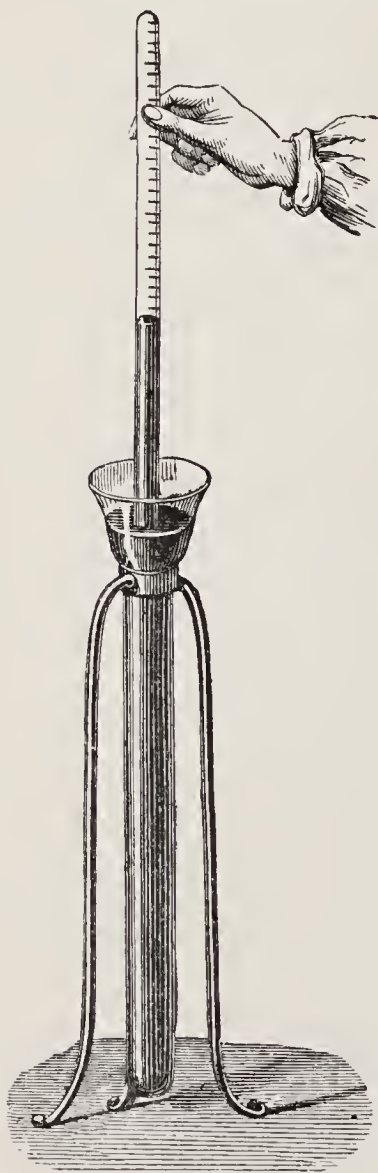


FIG. 52.

96. Maximum Pressure of Vapours.—The vapour in this condition—that is, when in contact with its liquid—is called “saturated vapour.” The vaporization just equals the condensation in any one of the above positions. If the space above the liquid be increased, more liquid vaporizes, until there is again equilibrium between vaporization and condensation.

By surrounding the tube B (Fig. 51) with a jacket, through which passes water at various temperatures, and noting the difference between the heights of the mercury in A and B, the maximum pressure of water vapour at various temperatures between 0° and 100° C. has been calculated.

By bending the tube, and dipping the end in freezing mixtures at various temperatures (Fig. 53), it has been shown that

even below zero water vapour exerts a pressure, its maximum pressure being definite.

The pressure in C is that due to the temperature of B, indicated by the thermometer t ; because the vapour from a layer of liquid in C is condensed in B, and the pressure in B is reduced, more vapour evaporates from C, to be further condensed in B. This continues until a state of equilibrium is reached, when the pressure in C is equal to that in B.

97. Regnault's Method.—Taking advantage of the fact, to be shown later, that when a liquid boils the pressure of the vapour is equal to the pressure to which it is subjected, Regnault has calculated the maximum pressure of aqueous vapour from 50° to 100° C. and upwards.

His method was to boil water in a vessel, and to subject it to various pressures. It was then only necessary to note the temperature when boiling took place. For example, when the pressure in the vessel was 39.27 lbs. on the square inch, the temperature of the water and steam in the vessel when boiling took place was 266° F.

Therefore the pressure of water vapour at a temperature of 266° F. is 39.27 lbs. on the square inch.

One form of the experiment is shown in Fig. 54.

Pure water was boiled in a copper vessel, C, fitted with delicate thermometers. The steam passed along the tube A B, and was condensed by the condenser D, supplied with cold water from E. The condensed water flowed back to C, and thus the operation could be continued without renewing the water. A B was connected with a glass globe, M, containing air kept at a temperature nearly that of the outside air

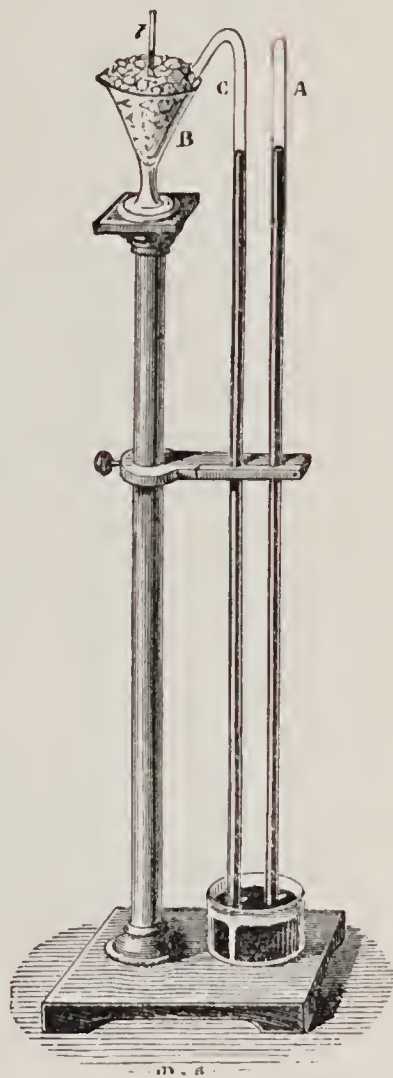


FIG. 53.

by water in the vessel K. M was connected with a manometer, O; M could also be connected by the leaden tube H H with either an air-pump or a force-pump.

(1) *Temperature below 100° C.*—H H was connected with an air-pump, and exhausted. The pressure was indicated by an

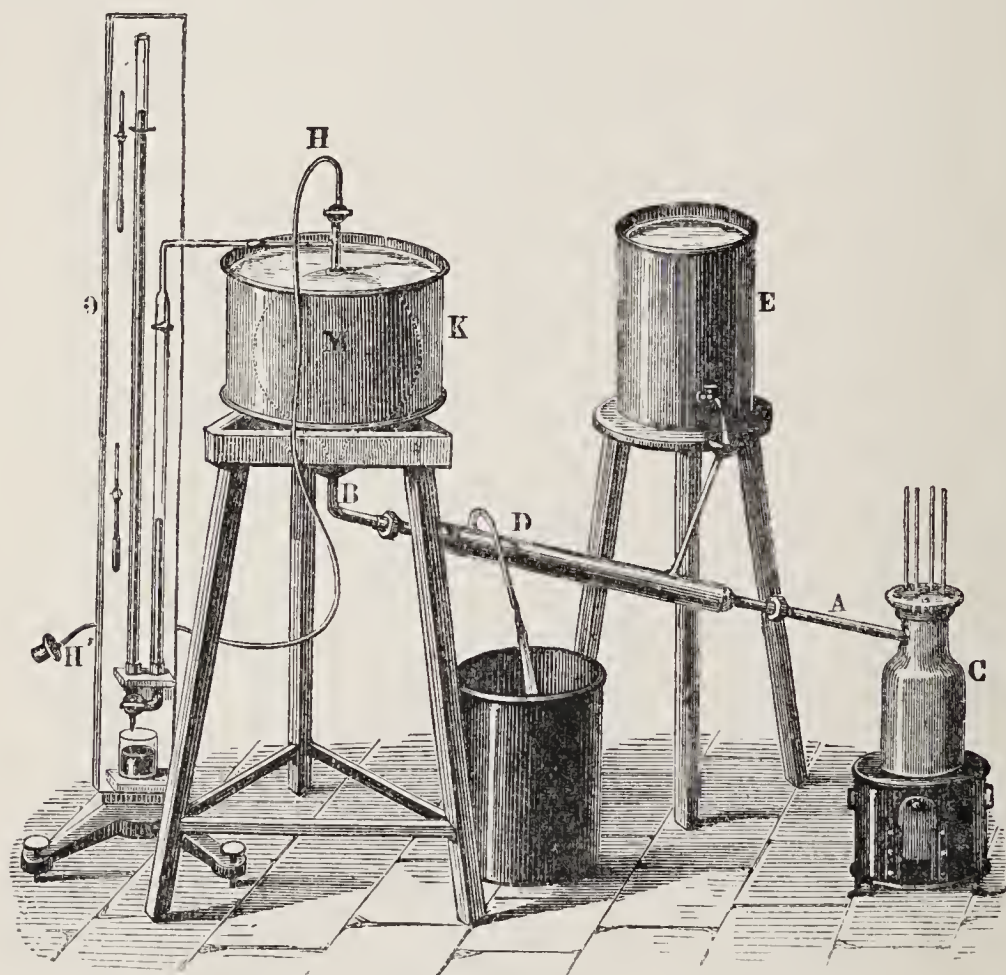


FIG. 54.

open manometer; it would be the pressure of the atmosphere less the difference in the lengths of the two columns of mercury. C is gradually heated, and boiling, known by the sound and the steadiness of the thermometer, takes place below 100° . A small quantity of air is admitted, the pressure changes, and another determination is made, and so on up to 1 atmosphere.

(2) *Above 100° .*—Air is forced into M. The mercury rises in the left-hand tube, as in the figure; the pressure = pressure of atmosphere + pressure due to difference in the columns of mercury. The boiling point is again observed. Such an arrangement would only serve for pressures to about $1\frac{1}{2}$ atmo-

sphere ; for higher pressures stronger apparatus was constructed, but the principle of the method remained the same.

MAXIMUM PRESSURE OF AQUEOUS VAPOUR IN MILLIMETRES
OF MERCURY.

— 10° C.	2.08 mm.	50°.	91.98 mm.	100°.	1 atmosphere
— 4°.	3.39 „	60°.	148.70 „	112.2°.	1½ „
— 2°.	3.95 „	80°.	354.64 „	120.6°.	2 „
0°.	4.60 „	98°.	707.26 „	133.9°.	3 „
10°.	9.20 „	99°.	733.91 „	152.2°.	5 „
20°.	17.40 „	100°.	760.00 „	180.3°.	10 „

In the following table the temperatures are given in degrees Fahrenheit, and the pressure in pounds per square inch:—

110°.	1.267	200°.	11.52	240°.	25.00
130°.	2.212	212°.	14.70	300°.	67.22
150°.	3.707	220°.	17.20	350°.	135.11

Complete tables, from which these are extracted, are of the utmost importance in questions relating to the strength of steam boilers.

By experimenting similarly with alcohol, ether, and other volatile liquids, their maximum pressures at various temperatures can be determined (use C, Fig. 51). Their pressures are much greater than water. Thus if ether were used, and the tubes were at 0°, the mercury would be depressed 182 mm.; alcohol at the same temperature would give a depression of 13 mm. At 10° C. the maximum pressure of ether vapour is 288 mm.; that of alcohol, 24 mm.

In all experiments, therefore, with volatile liquids the vapour pressure must be allowed for.

For example, suppose a gas is collected over water when the temperature is 20° C. Let the volume, after depressing the jar so that the level of the water inside the jar is equal to the level outside, be 25 c.cm., and let the corrected barometer read 750 mm.

The pressure inside the jar equals the pressure outside, which equals 750 mm. of mercury ; but the pressure inside is

made up of the pressure of the gas and the pressure of water vapour at 20°C .; this equals 17.4 mm. Therefore in any question relating to the gas we must consider it collected at 20° and at a pressure of $750 - 17.4 = 732.6$ mm. of mercury.

The vapour pressure of mercury below 100° is generally negligible, but is allowed for in very exact experiments; at 0°C . it is 0.02 mm., at 100° , 0.746 mm.

MAXIMUM PRESSURE OF MERCURY VAPOUR IN MILLIMETRES
OF MERCURY.

0° .	0.02 mm.	80° .	0.35 mm.	160° .	5.9 mm.
20° .	0.04 „	100° .	0.75 „	200° .	19.9 „
40° .	0.08 „	120° .	1.50 „	300° .	242.2 „
60° .	0.16 „				

The student should notice that, as a result of experiment, the maximum pressure of aqueous vapour at 100° (*i.e.* the boiling point) is equal to the pressure of the atmosphere. Similar experiments show that the maximum pressures of all liquids at their boiling points are equal to the atmospheric pressures to which they are subjected.

98. Vaporization in the Presence of other Gases.—

If the experiments be repeated, with the difference that dry air or any other dry gas occupies the Torricellian vacuum, a similar depression, with a maximum for each temperature, is shown, with the difference that the vapour takes a longer time to evaporate and exert its maximum pressure.

Dalton enunciated the following laws :—

(1) The maximum pressure of a saturated vapour depends only upon the temperature, and is not affected by the presence or absence of any other vapour that does not chemically affect it.

(2) The pressure exerted by a mixture of gases or vapours is equal to the sum of the pressures exerted by the individual gases or vapours.

The laws seem to be exact enough for most purposes, and in calculations it is assumed that they are true, as, for example, in meteorology.

99. Boiling.—If a liquid in a flask or beaker be heated from below by a lamp, or in any convenient manner, the following changes are observed: The temperature rises, and particles of air are expelled; there is also an increase in volume. The parts immediately above the lamp are the more heated; they expand, become less dense than the particles of equal volume above them, and therefore rise, others flow in from the sides, and a circulation ensues. The temperature at the bottom of the vessel is higher than the temperature of the upper layers, and bubbles of pure water vapour are formed; these bubbles rise and condense in the cooler layers above. The condensations follow each other rapidly, and probably cause the “singing” or “simmering.” General evaporation goes on from the surface throughout the process, increasing as the temperature rises.

Soon the general temperature is such (the temperature has risen throughout the process) that the bubbles of pure vapour are no longer condensed, and escape from the free surface. These are formed rapidly, and ebullition begins. The temperature in the case of water is now about 100°C. , but as soon as ebullition begins, no further rise takes place.

Boiling, unlike evaporation, is not confined to the free surface of the liquid. The change and interchange of molecules of liquid and vapour suggested in evaporation no longer take place.

In boiling, the molecules of vapour just formed chase the others away, driving out also the particles of air. The vessel above the liquid is now filled with molecules of water vapour, and the pressure of the vapour must evidently be equal to that of the atmosphere above it, which it supports. We thus deduce the following laws of ebullition:—

(1) The boiling point of any liquid is a temperature that is definite for a given pressure.

(2) The temperature of the boiling point remains constant as long as there is any liquid to vaporize, provided the pressure remains constant.

(3) The pressure of the vapour of a liquid during free ebullition is equal to the pressure of the atmosphere at the time.

TABLE OF BOILING POINTS UNDER NORMAL ATMOSPHERIC PRESSURE (C.°).

Oxygen	-182°	Petroleum ...	106°
Carbon dioxide	-80°	Acetic acid ...	120°
Chlorine	-34°	Aniline	180°
Sulphur dioxide...	-10°	Phosphorus ...	290°
Ether	35°	Sulphuric acid ...	326°
Wood spirit ...	66°	Mercury	350°
Alcohol	78°	Paraffin	370°
Water	100°	Sulphur	440°
Sea water ...	104°	Zinc	940°

The constancy of the boiling point for liquids may be readily verified by measuring the temperature of ebullition.

Even pure liquids, however, are affected by the nature of the vessel, and the temperature of each layer is not always the same. In determining the boiling point, therefore, the temperature of the vapour is noted.

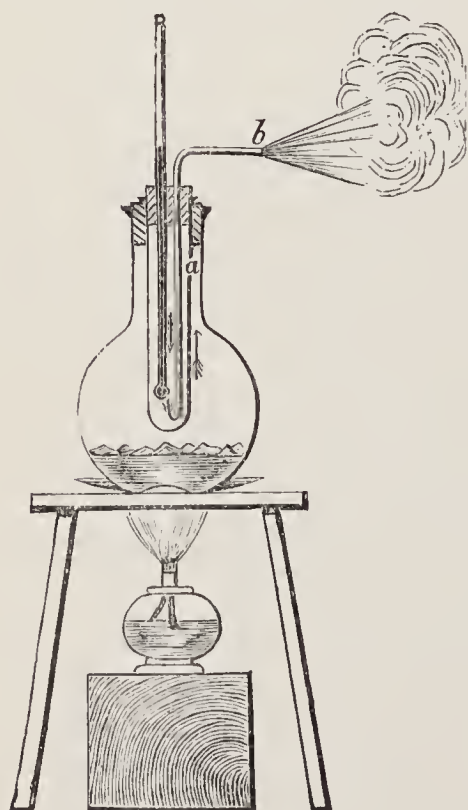


FIG. 55.

Fig. 55 can be conveniently used in determining boiling points, instead of the apparatus shown in Figs. 7 and 8. A small hole, *a*, is made in a test-tube. The test-tube is inserted in a clean flask containing the liquid. A bent tube, *b*, dipping nearly to the bottom of the tube, allows for the escape of the vapour (it should be wider than shown; the violent escape of steam in the figure suggests a notable increase of pressure inside the test-tube). By following the arrows it will be seen that the vapour in the test-tube

is kept from condensing by the vapour in the flask.

The reading of the thermometer will give the temperature

of the boiling point for the pressure of the atmosphere at that time, as given by the standard barometer.

The temperature of the boiling point for pressures near the normal atmospheric pressure has been determined with great accuracy. In determining the upper fixed point of a thermometer (§ 4) the point obtained is the temperature opposite the barometric pressure in the following table at the time of the experiment. For example, if at the time of the experiment the corrected barometric height was 754 mm., the point determined would be 99.8° C. ; if the barometer stood at 775, the point would be between 100.5° and 100.6° C.

PRESSURE OF AQUEOUS VAPOUR BETWEEN 99° AND 101° C.¹

			At 99° . mm.		At 100° . mm.
0.0	733.2	...	760.0
0.1	735.8	..	762.7
0.2	738.5	..	765.5
0.3	741.2	...	768.2
0.4	743.8	...	771.9
0.5	746.5	..	773.7
0.6	749.2	...	776.5
0.7	751.9	..	779.3
0.8	754.6	...	782.0
0.9	757.3	...	784.8

If, as in Fig. 17, the boiling point be simply determined, it is only necessary to connect the two tubes so that the steam has to overcome the pressure of a certain depth of water, or, better, of a certain depth of mercury, to show a rise in the boiling point due to an increase of pressure.

100. Effect of Pressure upon the Boiling Point.—Water may be made to boil at any temperature. The necessary and sufficient condition is that the pressure should be the pressure required for the given temperature (see Table, § 97).

Illustrations of water boiling at low temperatures are—

(1) Water is placed in a vessel under the receiver of an

¹ Kohlrausch's physical measurements.

air-pump; the vessel rests in a larger dish containing strong sulphuric acid. The air is exhausted, the pressure reduced, and evaporation of the water takes place, the vapour formed being absorbed by the sulphuric acid. When the pressure is lowered sufficiently the water boils. This classical experiment, due to Leslie, is not easy to perform. The sulphuric acid does not absorb readily, and the vapour spoils the tubes and valves connected with the air-pump. In all cases it is advisable to have the water slightly warmed.

(2) Another form of the same experiment is to boil water

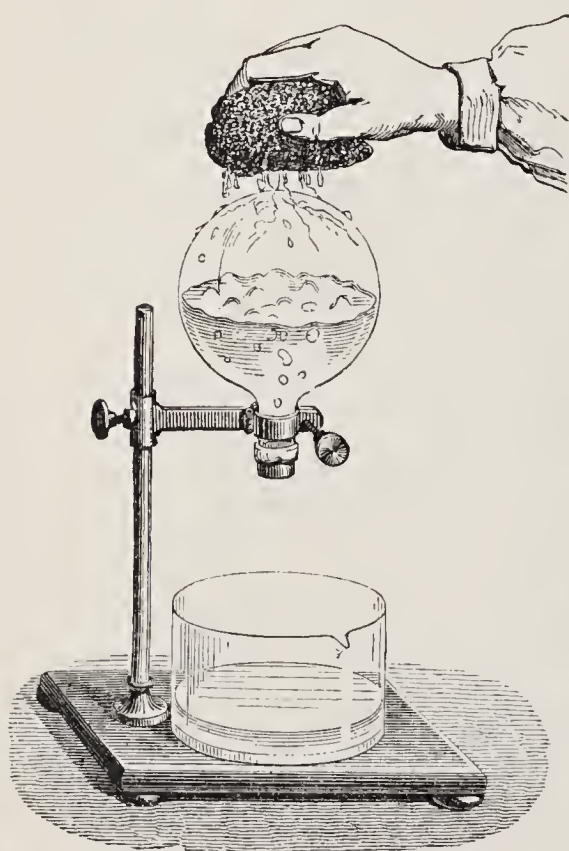


FIG. 56.

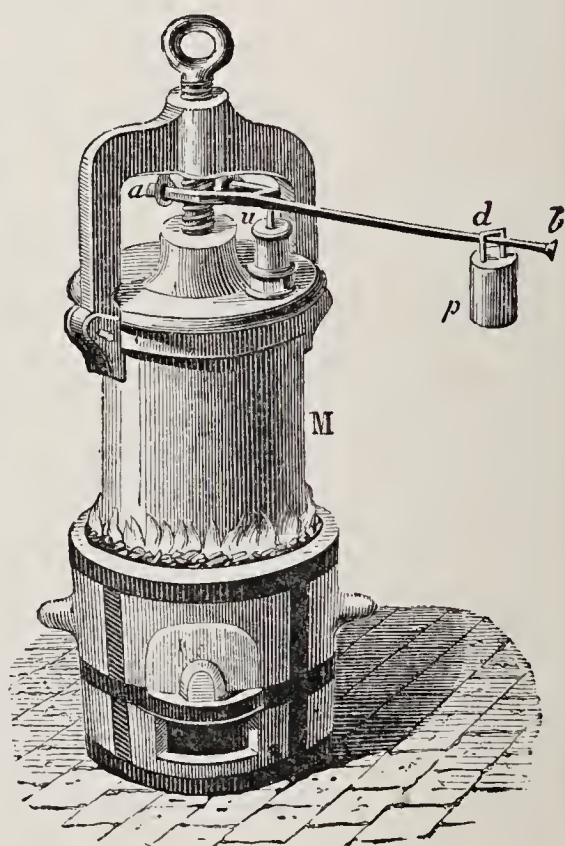


FIG. 57.

briskly in a flask; invert it, and allow it to cool. On pouring cold water over it, it begins to boil (Fig. 56).

The cold water condenses part of the vapour, and reduces the pressure inside the flask sufficiently to produce ebullition. Pouring hot water over it stops the boiling.

101. Papin's Digester.—Papin's digester (Fig. 57) is used for boiling liquids at high temperatures. The cover of the strong metallic vessel *M* is fastened down by a screw. The lever *b*,

whose fulcrum is at *a*, presses upon a rod, *u*, whose base is a valve pressing upon a hole in the cover. As the pressure increases it raises *u*, and the steam escapes. The pressure is regulated at from 5 to 6 atmospheres by the weight *p*, the amount is read from the graduated bar *d*; thus the boiling point will be between 150° and 160° C. At this temperature the gelatine can be extracted from bones. At high altitudes a modification can be used for cooking.

102. Hypsometers.—As we ascend, the pressure of the atmosphere diminishes, and therefore water boils at a lower temperature than 100° C. At Quito the boiling point is 90° ; on the top of Mont Blanc, 85.5° ;—temperatures insufficient for many cooking operations.

Travellers are able to use a hypsometer as a convenient way of determining altitudes. It consists of a copper vessel (Fig. 58) supplied with delicate thermometers, openly divided between 80° and 100° C., so that the tenths of a degree can be readily estimated. The vessel is telescopic, and, when closed, occupies small space.

Roughly, a diminution of 1° C. in the boiling point represents an increase in altitude of 1080 feet. For travellers, properly calculated tables are constructed; its portability gives it a great advantage over barometers, and clean snow is generally available.

103. Saline Solutions.—Salts dissolved in water raise the boiling point. The boiling point increases as the salt is added, until the solution is saturated and is unable to dissolve more.

In fixing the boiling point in the thermometer pure water was used. It was at one time thought that this was not neces-

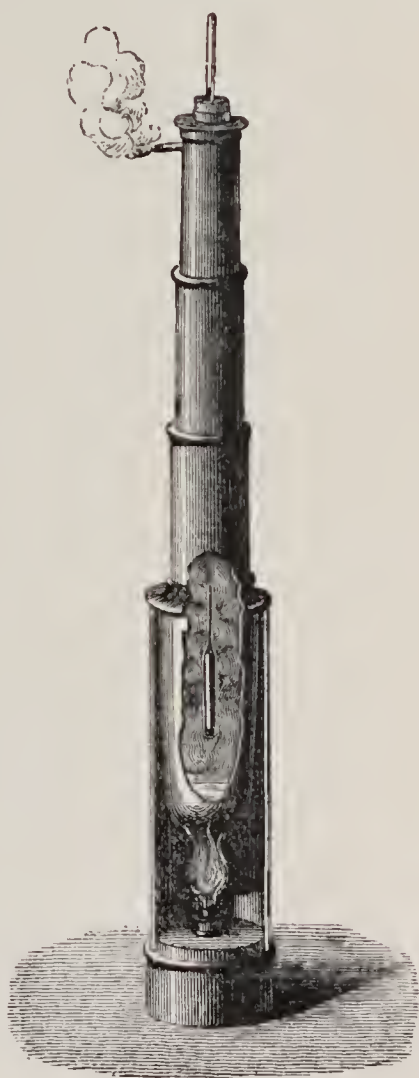


FIG. 58.

sary, as the steam from a saline solution was said to be at the temperature of boiling water boiling under the same pressure ; it seems, however, proved that it is higher.

The boiling point of a liquid is affected by the nature of the vessel ; water, for example, boils at a higher temperature in glass than in a copper vessel, the difference being about 1° . If the glass vessel be thoroughly cleaned, there seems a difficulty in boiling beginning, and sometimes the temperature will rise to 105° or 106° C., when it suddenly begins with "bumping." Boiling with "bumping" is avoided by adding pieces of metal (platinum) to the liquid.

Water freed from air by boiling and then allowed to cool can frequently be raised by reheating above 100° , in some cases up to 130° , before signs of boiling are shown, but, on boiling, the liquid is suddenly changed into vapour with explosive force.

104. Latent Heat of Vaporization.—During the time that boiling takes place, the temperature remains constant. The heat-energy is utilized in separating the molecules, so that the substance becomes a vapour. This energy exists as potential energy, and when the molecules close up in condensation, the heat-energy again appears as sensible heat. In the change from liquid to vapour there is a great increase in volume ; thus 1 cubic inch of water at 100° becomes 1700 cubic inches of steam at 100° . The vapour, therefore, if surrounded by air, say, has to force the air back, and in so doing does external work. The internal work is represented by overcoming the cohesion of the molecules, and in certain work, such as increasing the rotation, etc., of the molecules. This being done, if the source of heat be removed, the surrounding air presses upon the vapour and does work upon it, the molecules come closer together, the potential energy is liberated, and appears then as sensible heat.

The heat used during vaporization was said to be "latent ;" the real meaning can now be understood.

The number of units of heat required to change one unit of mass of a liquid at its boiling point into vapour without raising its temperature, is called the latent heat of vaporization of the liquid.

105. Dr. Black's Method.—Dr. Black made one of the first determinations by applying heat to a small quantity of water at 50° F. (suppose the mass to be 1 oz.), keeping the supplied heat as regular as possible. He noted the time that elapsed before the liquid boiled; still supplying heat, he noted how long it took to evaporate the water,—this latter operation took five times longer than it did to raise the water to boiling point.

He then argued that to raise a given mass from 50° to 212° requires 162 units (unit of mass 1 oz., degrees Fahrenheit); therefore to evaporate the mass takes $162 \times 5 = 810$ units. The method cannot give accurate results. No note is taken of the loss due to radiation and the loss of water due to evaporation, and his source of heat would vary. The method is instructive, and analogous to that followed in determining the latent heat of fusion (§ 82).

He next evaporated 1 lb. of water at its boiling point, and passed the steam formed through a spiral surrounded by 40 lbs. of water in a tube. The steam, in condensing, raised the temperature 20° , and he inferred that the latent heat of steam was 800. The result is again too low; but this method, modified, is still used in the methods of Despretz.

106. Modern Method.—The general plan followed at present is to allow the steam to pass directly into water; it is there condensed, and raises the temperature of the water. A simple form of the experiment can be made, avoiding small corrections, as follows:—

The flask A (Fig. 59) contains 300 grams of water; the temperature is 13° C. Water is boiled in C. The vapour passes along B and issues from D. When B and D are heated by the steam, and it issues freely, D is dipped into A. The steam condenses, heats the water in A. In four to five minutes the temperature rises to 52° C. D is removed, and A is weighed. The increase is found to be 20.2 grams. A bright sheet of tin prevents radiation between the two flasks, and B catches condensed water and prevents it passing along D.

(1) 300 grams are heated through 39 degrees. This requires $300 \times 39 = 11,700$ thermal units.

(2) This is supplied by (a) 20.2 grams of steam at 100° passing into liquid at 100° ; and (b) 20.2 grams of water

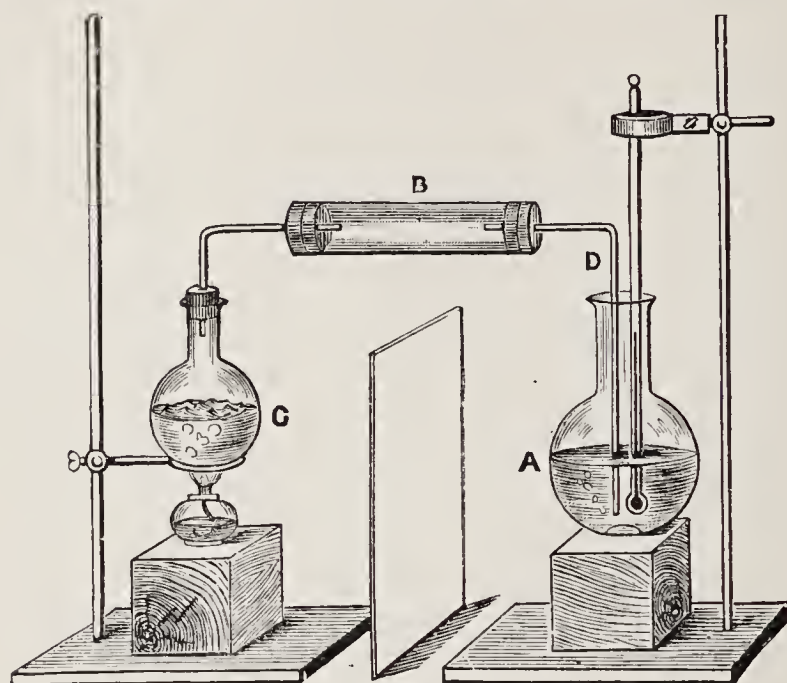


FIG. 59.

cooling from 100° to 52° . (b) gives up $20.2 \times 48 = 969.6$ thermal units.

$11,700 - 969.6 = 10,730.4$ thermal units must be supplied by 20.3 grams of steam condensing.

\therefore 1 gram of steam condensing gives up $\frac{10,730.4}{20.2} = 534$ thermal units

The latent heat of evaporation is 534 (in accurate experiments it is 537). There are many obvious causes of error, due to radiation, to water passing over, and to water condensing in D.

Precaution must be taken to see that the steam in D is not cooled. It should pass through a copper spiral enclosed in a steam-jacket; the steam in the spiral will thus be kept at 100° C. The calorimeter should be similar to that shown in Fig. 41, but larger, its water equivalent being known.

Let M = mass of water in the calorimeter; ω its water equivalent.

t = initial temperature of the calorimeter.

θ = final " " "

m = mass of steam condensed.

L = latent heat of steam.

(1) The mass of steam, m , at 100° condenses to water at 100° , and liberates mL units of heat.

(2) m units of water cool from 100° to θ , and liberate $m(100 - \theta)$ units of heat.

(3) The water in the calorimeter and the calorimeter gain $(M + \omega)(\theta - t)$ units of heat.

$$\therefore mL + m(100 - \theta) = (M + \omega)(\theta - t)$$

$$\therefore L = \frac{M + \omega}{m}(\theta - t) - (100 - \theta)$$

If the temperature of the steam be T instead of 100° (for example, if the barometer stood at 750 mm., it would be 99.63° by § 99), then the exact value must be substituted for 100 in the above equation.

107. Total Heat of Steam.—Regnault made a large number of experiments in order to determine the total heat necessary to raise 1 unit of mass of water at freezing point to any given temperature, and to evaporate it at that temperature. This is called the “total heat of steam.” If the given temperature be 100°C. , then the two quantities are roughly $100 + 537 = 637$ thermal units.

Regnault concluded that the total heat could be obtained at any temperature from the formula—

$$\text{Total heat} = 606.5 + 0.305t$$

where t is the temperature in degrees Centigrade. The total heat increases with the temperature.

At 100° the total heat is $606.5 + 30.5 = 637$.

If the experiment be conducted so that the water is finally evaporated at 50° (that is, the pressure must be 91.98 mm.)—

$$\text{The total heat} = 606.5 + 15.25 = 621.75 \text{ thermal units}$$

The total heat of steam is given in tables for a wide range of temperature, and therefore, knowing the heat required to raise unit of mass from 0°C. to the given temperature (*i.e.* determine the specific heat between the two temperatures), the latent heat of evaporation can be calculated at any temperature.

$$\begin{aligned}
 \left. \begin{array}{l} \text{Total heat} \\ \text{at } t^\circ \end{array} \right\} &= \left\{ \begin{array}{l} \text{Specific heat} \\ \text{from } 0^\circ \text{ to } t^\circ \end{array} \right\} + \left\{ \begin{array}{l} \text{Latent heat of} \\ \text{vaporization at } t^\circ \end{array} \right\} \\
 T &= S + L \\
 \text{also } T &= 606.5 + 0.305t \\
 \therefore L &= T - S = 606.5 + 0.305t - S
 \end{aligned}$$

Assuming that the average specific heat between 0° and t° is unity—

$$\therefore L = 606.5 - 0.695t$$

$$\begin{aligned}
 \text{The latent heat at } 0^\circ &= 606.5 \\
 \text{,, ,, } 10^\circ &= 599.55 \\
 \text{,, ,, } 100^\circ &= 537
 \end{aligned}$$

The latent heat diminishes as the temperature increases.

We can calculate the temperature at which the latent heat is zero, by making L equal to zero; then—

$$\begin{aligned}
 0 &= 606.5 - 0.695t \\
 \therefore t &= \frac{606.5}{0.695} = 866^\circ \text{ C.}
 \end{aligned}$$

This temperature is far above that of any possible experiment with steam, and we cannot, therefore, attach any particular value to it. It suggests, however, that at some particular temperature the liquid will pass instantaneously into vapour. The student should refer to this after § 117.

The student will find no difficulty in understanding how vaporization takes place at any temperature. At 100° the pressure will be 760 mm. of mercury; at 50° the pressure will be 92 mm.; at 150° C. the pressure will be 5 atmospheres; and at 0° the pressure will be 4.6 mm.

The particulars relating to water in its three states can now be conveniently collected.

	Specific heat.	Latent heat.	Temperature of change under constant pressure.
(1) Solid: <i>ice</i>	... 0.504 (from -20° to 0° C.)	... 80	... 0°
(2) Liquid: <i>water</i>	1	... 537	... 100°
(3) Vapour: <i>steam</i>	0.4805		

$$\text{Total heat of steam} = 606.5 + 0.305t$$

$$\text{Latent heat at } t^{\circ} = 606.5 - 0.695t$$

108. Latent Heat of other Liquids.—The following table gives the latent heats at normal pressure and at their ordinary boiling points. The latent heat of steam is very large compared with the other liquids, and explains the heat and time necessary to change water into its vapour compared with the heat and time required to change any other liquid. In nature the evaporation (the latent heat below 100° is greater than at 100°) of water takes place slowly, and when water vapour condenses to water there is a great liberation of heat-units, explaining the rise in temperature which follows rain, and the severe scalds from steam.

			Boiling point.		Latent heat of vaporization.
Water	100°	...	537
Alcohol	78°	...	202
Sulphur dioxide	-10°	...	97
Carbon disulphide	48°	...	87
Ether	38°	...	80
Turpentine	159°	...	74
Mercury	350°	...	62
Chloroform	85°	...	61

109. Coldness due to Evaporation.—If the heat necessary for evaporation of a substance be not supplied by an external source of heat, it will be taken from the substance itself or the bodies near it, and the temperature will fall. To this is due the coldness felt when water, alcohol, ether, or other volatile liquids evaporate from the hand.

The temperature of a room is lowered by sprinkling water on the floor, the heat required for evaporation being taken from the temperature of the air. Porous water-vessels keep the water they contain cool by the evaporation from the outside surface. The evaporation of the perspiration from the skin keeps the body cool, and if a volatile liquid such as eau-de-Cologne be used, the reduction of temperature takes place more rapidly; its latent heat of evaporation is not so great,

but at the ordinary temperature it is nearer its boiling point than water, and evaporation takes place the more readily. The heat liberated in condensation is utilized in manufactories; liquids are readily heated by passing steam through them.

110. Internal and External Work in Vaporization.—The energy given to the liquid has—

(1) To do internal work in overcoming the cohesion of the molecules.

(2) To do external work in expanding the liquid against the pressure of the atmosphere.

This has already been simply discussed in § 78. It will form a good exercise to do it here with greater accuracy.

$$\begin{aligned} 1 \text{ volume of water at } 4^{\circ} \text{ C.} &= 1.0001 \text{ at } 0^{\circ} \text{ C.} \\ &= 1.0008 \text{ at } 15^{\circ} = 1.0432 \text{ at } 100^{\circ} \text{ C.} \\ &= 1696 \text{ volumes of steam at } 100^{\circ} \text{ C} \end{aligned}$$

the pressure throughout being that of the normal atmosphere
= 14.7 lbs. on the square inch.

$$\therefore 1 \text{ volume of water at } 100^{\circ} \text{ C.} = 1624 \text{ volumes of steam at } 100^{\circ} \text{ C.}$$

To vaporize 1 lb. of water at 100° C. takes 537 heat-units
= $537 \times 1390 = 746,430$ foot-pounds of energy.

1 cubic foot of water at 100° C. weighs 59.64 lbs.

$$\therefore 1 \text{ lb. of water will represent } 29 \text{ cubic inches}$$

If now we imagine the 1 lb. of water in a cylinder whose section is 29 square inches, it will stand at 1 inch in the tube, and when vaporized will stand at 1624 inches.

The pressure on the water is $14.7 \times 29 = 426.3$ lbs.

$$\begin{aligned} \therefore \text{external work done} &= 426.3 \times \frac{1623}{12} \text{ foot-pounds} \\ &= 57,665.4 \text{ foot-pounds} \end{aligned}$$

$$\begin{aligned} \therefore \text{internal work} &= 746,430 - 57,665.4 \\ &= 688,764.6 \text{ foot-pounds} \end{aligned}$$

$$\begin{aligned} \therefore \text{external work} : \text{internal work} &:: 57,665.4 : 688,764.6 \\ &= 1 : 11.9 \end{aligned}$$

111. Ice-Machines.—In Leslie's experiment (§ 100), if the exhaustion be continued far enough, and the sulphuric acid absorbs the moisture, the liquid not only boils, but its temperature falls so that it freezes. A practical modification of this is Carré's ice-machine (Fig. 60).

A strong cylinder, R, contains strong sulphuric acid introduced by the funnel E. P is an air-pump that exhausts air

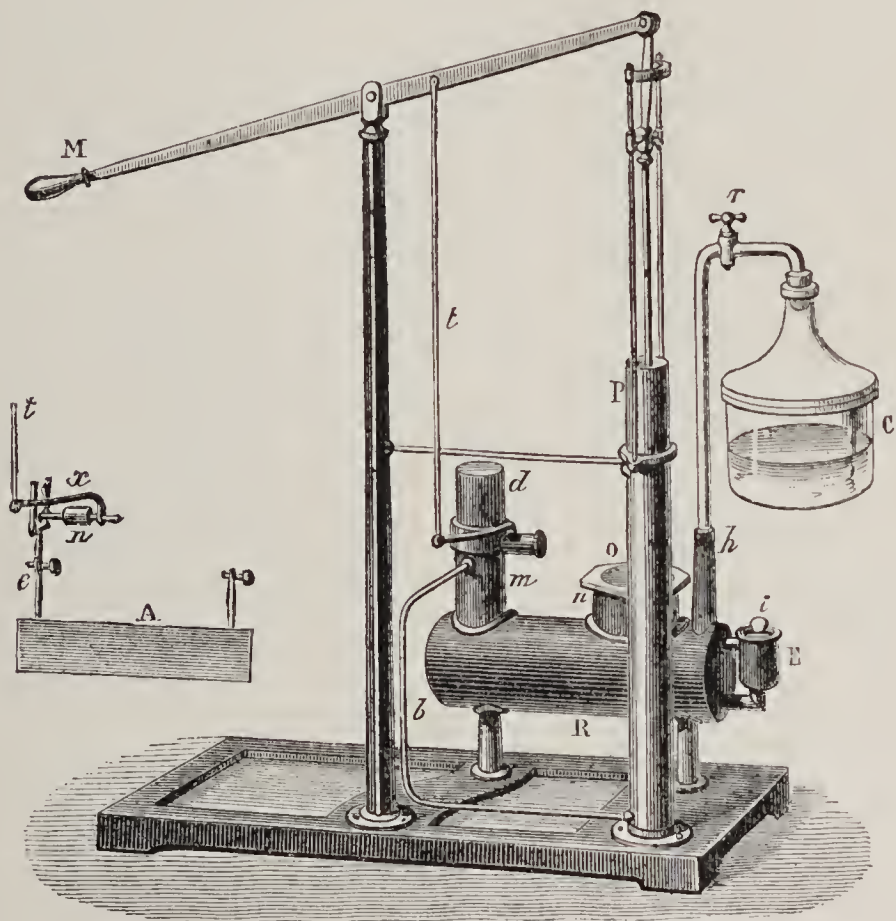


FIG. 60.

from the cylinder by the pipe *b*, connected with R by the tubulure *m*. The dome *d* above *m* supports obstacles to prevent the spurting of acid into *m* and *b*. The pump is worked by a lever, M, which at the same time moves a rod, *t*, that keeps in motion a stirrer, A, in the liquid (the mechanism is shown at A, the intermediate parts being *x*, *n*, and *e*). A wide tube, *n*, is covered by a glass disc, O, and through the glass the movement of the acid can be observed. The interior of the cylinder is connected with the bottle

containing the water to be frozen, by a tube, *h*, in which is inserted a stop-cock, *r*. On pumping, the pressure is reduced, and the water in C evaporates. It is the more readily absorbed, seeing that the acid is stirred. Soon the water boils. When this stage is reached, a few strokes at intervals of a few minutes continue the evaporation, and the water freezes.

The principle is equally well illustrated in the following experiment: A thin copper capsule, C (Fig. 61), is rested on some water spilt upon a board, B. Carbon disulphide is placed in the capsule, and evaporated by blowing over it with

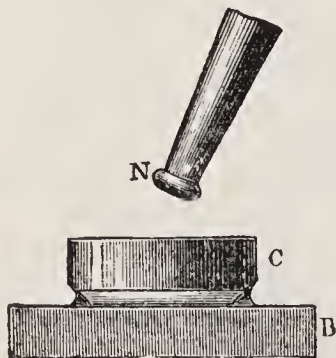


FIG. 61.

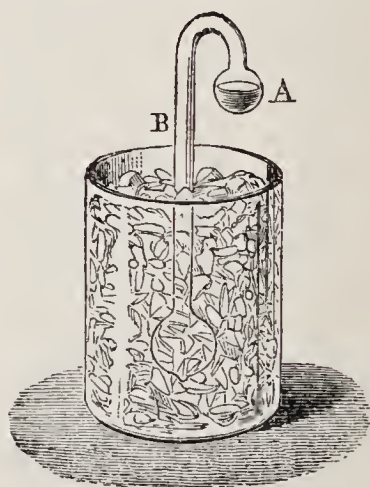


FIG. 62.

a pair of bellows, N. Its temperature falls so much that the water beneath the capsule freezes. This should be performed in the open air.

Wollaston's cryophorus (Fig. 62) consists of two bulbs connected by a bent tube, B. Water is placed in it and boiled briskly. It is then hermetically sealed, so that it contains only water and its vapour.

All the water is placed in A, and the other bulb is placed in ice or some suitable freezing mixture. The evaporation from A soon reduces the temperature so far that dew, and then snow, forms on the outside; ultimately the water in A freezes.

112. Freezing of Mercury.—To effect this a temperature of -40° C. must be obtained. Liquid sulphur dioxide boils at -10° C. If the bulb of a small thermometer be covered

with cotton wool which is moistened with sulphurous acid, then, if it be placed under the receiver of an air-pump, and the pump be exhausted, the rapid evaporation lowers the temperature below -40° , and the mercury is frozen.

By selecting liquids that are extremely volatile, very low temperatures can be produced. The application of this will be seen in the liquefaction of gases.

113. Evaporation.—The conditions favourable to evaporation are—

(1) *The area of the free surface.*—Advantage is taken of this in evaporating large masses of liquid. For example, salt-pans are made as large and as shallow as possible. A similar plan is followed in evaporating salt water on the sea-coast.

(2) *The pressure.*—Dalton demonstrated the relation by supporting a dish of water at 45° F. over a dish of concentrated sulphurous acid, and placing all under the receiver of an air-pump. He allowed evaporation to go on for 30 minutes, keeping the pressure constant for each experiment, and then, by weighing, he calculated the mass of water that had evaporated. His experiments showed that the loss due to evaporation was inversely as the pressure: when the pressure was 30.4 inches of mercury, 1.24 gram evaporated; when the pressure was 15.2 inches, 2.97 grams evaporated.

In § 95 it has been shown that when evaporation takes place *in vacuo*, the rate is almost instantaneous.

(3) *The pressure due to two vapours* is equal to the sum of the pressures of the vapours when acting separately. Evaporation takes place independently of the presence of other vapours, but the rate is slower (§ 98).

If a vapour evaporates into a confined space, the limit will be due in all cases to the pressure of its own vapour. The greater the amount of vapour already in the space, the slower will be the rate of evaporation; and as each particle evaporated increases the amount in the space, the slower will be the next small quantity in evaporating.

We see, therefore, that any circumstance that will remove vapour when formed will assist evaporation. Evaporation will

take place more readily in dry air than in moist air; it will be assisted by winds removing the moist air;—facts noticeable in nature. The removal of the moist air by absorption is the function of the sulphuric acid in Leslie's and Carré's machines.

The greater the pressure of the vapour of the liquid, the more readily will it overcome the resistance of any gas or vapour present, and the more rapid will be the evaporation. We increase the pressure by raising the temperature, and it is well known that evaporation is assisted by raising the temperature of the liquid as nearly as possible to the boiling point.

The whole subject will be further illustrated in the chapter on climate.

114. Sublimation.—Reference has already been directed to the fact that ice disappears from the streets without passing into the liquid state; at any rate, we are unable to detect the formation of liquid. This process is called *sublimation*. It can be illustrated by heating iodine or ammonium chloride in a test-tube. The gradual disappearance of solid camphor is a further illustration.

115. Distillation.—Distillation is another illustration of evaporation and condensation. Evaporation is produced ordinarily by the heat from a lamp; the vapour passes from a region of high pressure to one of lower pressure, and is condensed, the condenser being kept cold by running water. Liebig's is a well-known form of laboratory condenser (Fig. 63).

The condenser *j* is a glass tube that surrounds another tube, *g*; the ends of *j* are made water-tight by rings of indiarubber tubing. The condenser is kept cold by water entering at the lower end after passing through the funnel *f* and the tube *B*, and leaving it (warmed, of course, since the latent heat of vaporization becomes sensible in condensation) at the upper end by the tube *t*. The liquid is placed in a retort, *A*, the stem of which fits tightly into *g*, which, in its turn, fits loosely into the receiver *C*, in which the condensed liquid collects. In some apparatus the vapour passes through a worm kept in a large vessel of cold water.

For many purposes (as sugar-refining) a high temperature

would be fatal to success. Distillation is then attained by reducing the pressure, thereby introducing evaporation at lower temperatures (§ 100).

116. Fractional Distillation.—If a number of volatile liquids that do not chemically combine be mixed together, the substance with the lower boiling point distils at that lower

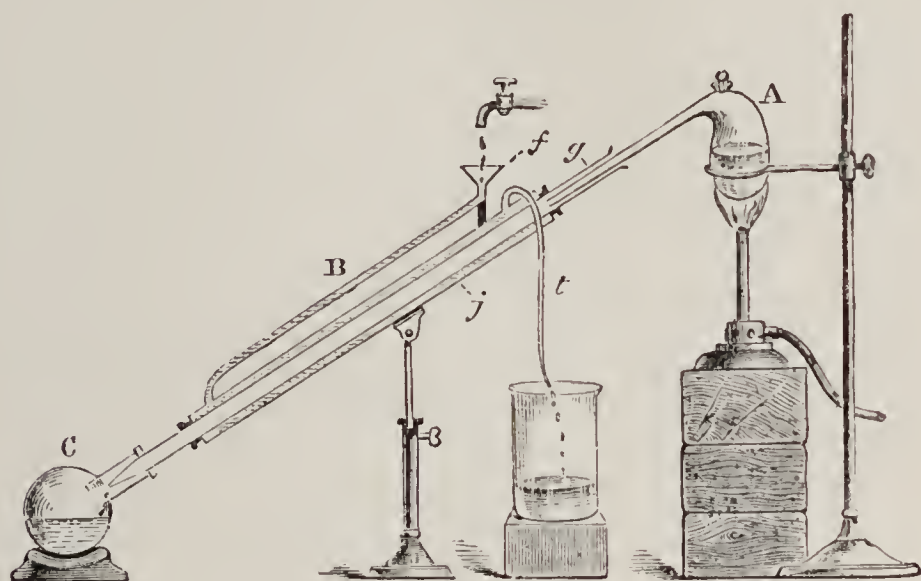


FIG. 63.

temperature at a greater rate than the others. If a mixture of alcohol and water be distilled slowly, the first distillate up to the boiling point of alcohol (80°C.) contains the greater proportion of the alcohol. If this be again distilled, a distillate stronger in alcohol is obtained. This is termed “fractional distillation.” By its aid liquids with different boiling points can be roughly separated. Seeing that evaporation of liquids goes on at all temperatures, pure substances cannot be obtained by this process alone.

WORKED EXAMPLES.

1. The specific heat of mercury is 0.03 . A pound of steam at 100°C. is made to pass into a vessel containing 300 lbs. of mercury initially at 0°C. , the capacity for heat of the vessel being equal to that of 10 lbs. of water: what will be the temperature of the vessel and the contents at the end of the experiment? Latent heat of steam is 537. (Lóndon Matric.)

Let t = temperature.

(1) Water loses $537 + (100 - t)$ heat-units.

(2) Mercury and vessel gain $(300 \times 0.03)t + 10t$ heat-units.

$$\therefore 537 + 100 - t = 9t + 10t = 19t$$

$$\therefore 20t = 637$$

$$\therefore t = 31.85^\circ \text{C.}$$

2. A barometer tube is filled with mercury and inverted over mercury. At first the column stands at 754 mm., and agrees with the standard barometer. The vacuum measures 50 mm. Dry air is forced up until the column measures 724 mm., and then water is forced up the tube until a thin layer forms; the mercury column is depressed and measures 700.6 mm. Calculate the maximum pressure of aqueous vapour at the temperature of the room, 10°C .

(1) The dry air occupies $50 + 30 = 80$ mm. of the tube, and is subject to a pressure of $754 - 724 = 30$ mm. of mercury.

(2) After the water vaporizes, the volume of the air is $30 + (724 - 700.6) = 53.4$.

$$\therefore \text{pressure} = \frac{30 \times 80}{53.4} = 44.9$$

(3) The pressure of the aqueous vapour (x) + the pressure of the air + the pressure of 700.6 mm. of mercury balances the pressure of the atmosphere = 754 mm.

$$\therefore x + 44.9 + 700.6 = 754$$

$$\therefore x = 8.5 \text{ mm.}$$

EXAMPLES. VII.

1. How is "latent heat" explained by the dynamical theory of heat?
2. Describe the cryophorus, and explain the principle of its action.
3. If the latent heat of vaporization be 537 when one degree Centigrade is the unit of temperature, what will it be when one degree Fahrenheit is the unit? Would your result be different if the unit of mass were changed?
4. If 30 grams of steam at 100°C . be passed into 400 grams of ice-cold water, what will be the temperature of the mixture, assuming the latent heat of steam to be 537?
5. At the sea-level the barometer stands at 750 mm., and the temperature 7°C ., while on the top of a mountain the barometer stands at 400 mm., and the temperature -13°C .: compare the weights of a cubic metre of dry or of saturated air in the two places.
6. How would you proceed to determine the maximum pressure of the vapour of a mixture of sulphuric acid and water at various temperatures?
7. Find the temperature after mixing (a) 2 lbs. of ice at 0°C . with 7 lbs. of water at 50° ; (b) 4 lbs. of ice at -10°C . with 30 lbs. of water at 20° , and passing 1 lb. of steam into the mixture.
8. Find the total heat of steam at 60° and at 100°C .
9. How much steam must be approximately passed into 4 gallons of water at 60°F . to raise the temperature to 180°F .?
10. Steam is passed through a copper worm placed in a calorimeter.

The worm weighs 20.5 grams; its specific heat is 0.095. The calorimeter is also of copper, and weighs 40 grams; it contains 250 grams of water, and the initial temperature is 12°C . The temperature of the steam is 100°C . 3.32 grams of steam are condensed, and the condensed water leaves the worm at a temperature of 20°C ., being the final temperature of the calorimeter. Calculate the latent heat of steam.

11. Describe Regnault's method of determining the maximum temperature of water vapour. 300 c.cm. of hydrogen are collected over water. The corrected barometer reads 750 mm., and the temperature is 20°C . The water is at the same level inside and outside the tube. Calculate the volume of dry hydrogen at normal temperature and pressure.

12. What effect has pressure upon the boiling point of a liquid? How would you experimentally illustrate your answer?

13. A steam heating apparatus is worked with a boiler that indicates a pressure of 20 lbs. on the square inch: find the temperature of the steam in the boiler. What will it be when the pressure rises to 30 and 40 lbs. per square inch?

CHAPTER VIII.

LIQUEFACTION OF GASES—VAPOUR-DENSITIES.

117. Isothermals for Steam.—An isothermal for air (§ 42) forms for all practicable pressures a continuous curve. In the case of steam or any vapour that can be condensed we obtain an isothermal that is not continuous. Let us examine the case of steam at 100°C . If the pressure at the beginning be considerably below 1 atmosphere—say a pressure equal to a column of mercury 200 mm. in height—then, if we slowly increase the pressure, keeping the temperature constant, and record the results graphically, we form at first an isothermal that is nearly a rectangular hyperbola. As the pressure is increased, the curve, instead of continuing to agree with the hyperbolic curve, falls below it; that is, the volume is less than it should be if calculated according to Boyle's law. This decrease in volume continues as we approach a pressure of 760 mm. When the pressure is 760 mm., or 1 atmosphere, the steam is on the point of being condensed. The short limb of the Boyle tube (Fig. 33) could be surrounded by a steam-jacket kept at 100°C .; the mercury in both limbs would be level when the pressure is 1 atmosphere (§ 100). If now we attempt to increase the pressure by pouring mercury into the long limb, we observe that the mercury in both limbs continues level, showing that, although the volume of steam is decreasing, the pressure is keeping constant at 1 atmosphere. The other observable effect is that part of the vapour is condensing, and a layer of water is formed. The isothermal up to the point when condensation begins is the curve *a b*

(Fig. 64). With diminished volume we have constant pressure

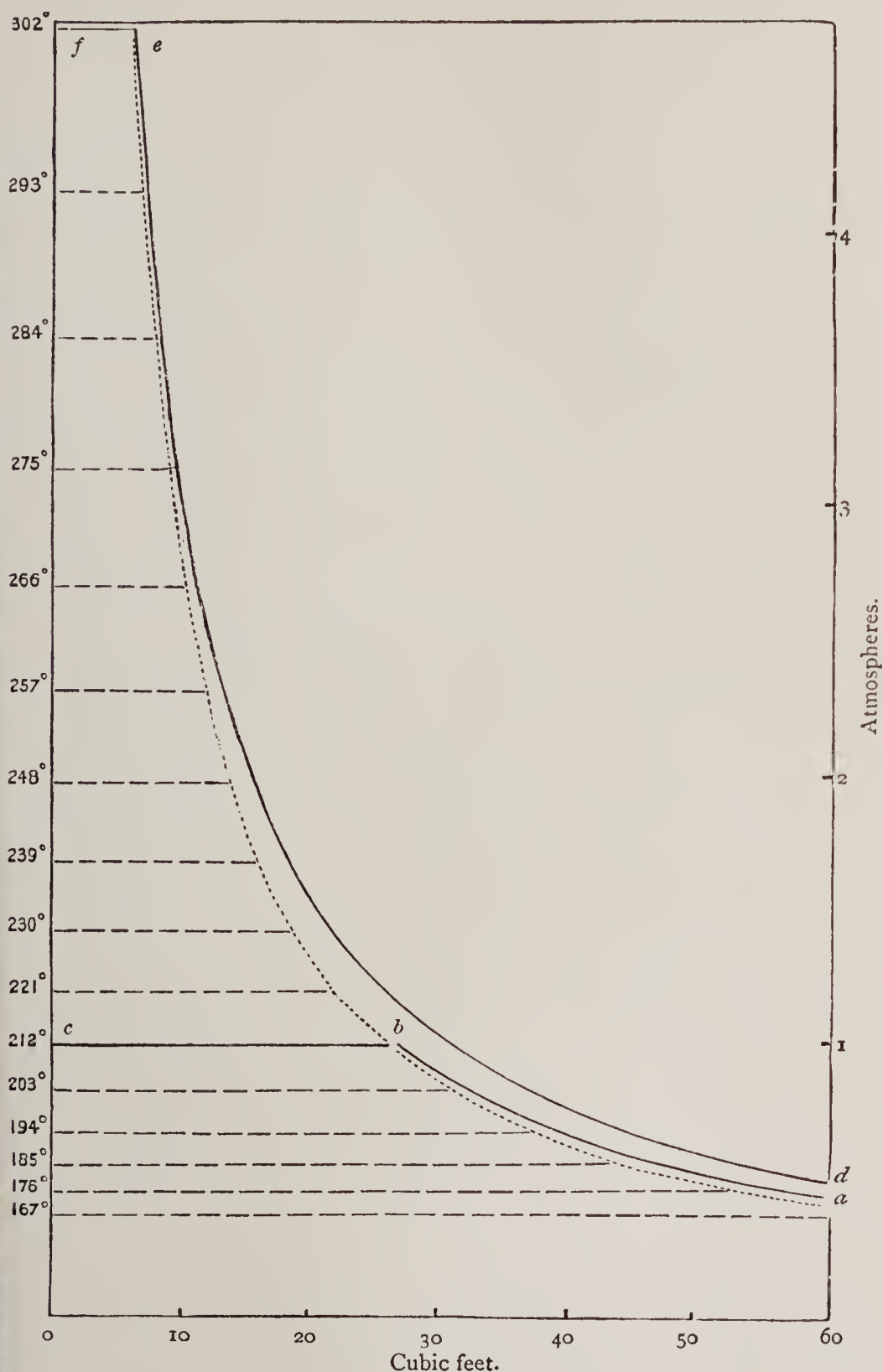


FIG. 64.

represented by the horizontal line *bc*. This simply represents

the fact that at 100 C. (212° F.) the maximum pressure of water vapour is 1 atmosphere, and no higher pressure is possible as long as the temperature is 212° F.

In the diagram the isothermals are for 1 lb. of steam. Volume is measured in cubic feet, and pressure in atmospheres. When the volume becomes 0·016 cubic foot (too small to be represented on the figure), the whole of the steam is condensed; and to continue the curve would give the isothermal of water at 212° F. It requires enormous pressure to produce any appreciable diminution of volume; so that the curve from *c* would be almost vertical. If the isothermal for 302° F. be drawn, we find from the tables that the maximum pressure of water vapour at that temperature is 69·27 lbs. on the square inch, equal to $\frac{69\cdot27}{14\cdot70} = 4\cdot7$ atmospheres. The isothermal up to this pressure is *de*, the volume of steam being 6·153 cubic feet. The pressure now remains constant until the whole is condensed into water at 302° F., when the volume is 0·0176 cubic foot.

If we took the temperature at 356° F., the volume at the point where condensation begins would be 2·025 cubic feet, the pressure being 10 atmospheres. When condensation is completed, the volume is 0·018 cubic foot of water.

Temperature F.	Maximum pressure in lbs. per square inch.	1 lb. of steam. Volume in cubic feet.	
		(a) When at maximum pressure.	(b) Of water formed.
212°	14·70	26·360	0·0167
302°	69·27	6·153	0·0174
392°	226·07	2·025	0·0183
401°	250·57	1·838	0·0184

We notice that, as the temperature increases, the volume of steam before condensation is approaching the volume of water formed, suggesting that at some very high temperature, probably beyond experiment, the volume of steam would be so nearly equal to the water formed that it would be difficult

to detect the difference; that is, the density of steam before condensation is approaching the density of the water formed.

The latent heat of steam is also decreasing (§ 107). At 212° it is 965.7; at 392° it is 838; and thus a smaller quantity of heat is necessary to effect the change from liquid to vapour;—liquid and vapour are approaching a state of unstable equilibrium. It will be seen that with other substances we are able to reach a state when this unstable equilibrium is more marked.

Steam at pressures very much lower than the maximum pressure at which it can condense acts like a perfect gas, and the relation $PV = \text{constant}$ is approximately true. The steam must, however, be thoroughly superheated.

When near its point of condensation the formula which represents the relation of pressure and volume is—

$$PV^{\frac{17}{16}} = \text{constant}$$

a formula of great use in questions relating to steam-engines.

118. Liquefaction of Gases.—Many bodies are known to us both in the liquid and gaseous forms. At ordinary pressures water is liquid below 100° C., and vapour above that temperature. Alcohol is liquid below 80° C., and vapour above it. Ether is liquid at 35° C., and vapour above. Sulphur dioxide, but that we possess means of obtaining low temperatures, would only be known as a vapour, since it is only liquid at temperatures below -10° C. under ordinary atmospheric pressure; and, therefore, in some Arctic regions, would be generally known as a liquid with a low boiling point.

This suggests one general method of experimenting upon gases with a view to liquefying them, namely, by reducing the temperatures.

The boiling point is raised by increasing the pressure. Assuming that any substance ordinarily known to us as a vapour can exist as a liquid, we see that the boiling point must be at some temperature lower than that it is usually subjected to. But increase of pressure raises the boiling point; it is therefore fair to infer that, if we increase the pressure of

a gas, it may be possible to so raise its boiling point that the gas may exist as a liquid.

The two methods—(1) lowering the temperature, (2) increasing the pressure, or combinations of both, have been the methods followed in liquefying gases.

The liquefaction of water vapour can be readily shown by modifying the apparatus of Fig. 51. The amount of water formed is small, and will be the more readily seen if the upper part of the tube be drawn out for 2 or 3 inches, to make it much narrower, and then closed, taking care to keep the glass thick enough to resist the pressure. It is filled completely with pure dry mercury, and inverted in the usual way. A few drops of water are forced up, insufficient to form a layer; that is, so that the whole vaporizes. If the temperature of the room be 20° C. say, then the mercury can be depressed about 15 mm. (maximum pressure = 17.4 mm.; see Table, § 97) without a layer of water forming. The pressure will be approximately 15 mm. of mercury. Remove the tube to the deep trough (Fig. 52), and slowly depress the tube; that is, increase the pressure on the vapour. When the pressure exceeds 18 mm., the water will begin to condense, and the small quantity formed can be seen in the narrow part of the tube. By further depressing the tube, the whole can be liquefied. If at the beginning a small layer forms, it can be vaporized by surrounding the upper part of the tube with another tube, and pouring warm water into the second tube. Suppose the water is at 60° C., then the depression produced will be about 149 mm. Still keeping it surrounded with the warm water at 60° , depress it in the deep trough, and the water vapour will be condensed.

By raising the tube rapidly, the boiling of the liquid under reduced pressure can be observed.

Or when the water has just been vaporized by the heat from the warm water, if the warm water be run off, condensation (liquefaction) takes place by cooling, and the mercury rises in the tube.

Ether can be treated similarly, save that the jacket of warm water is unnecessary, and that, to show liquefaction by lowering the temperature, ice-cold water should be used.

Sulphur dioxide, as made in the laboratory, is a gas. If it be subjected to a temperature below -10° C. at the ordinary pressure, it becomes liquid.

The gas is generated in the flask A (Fig. 65), and is passed

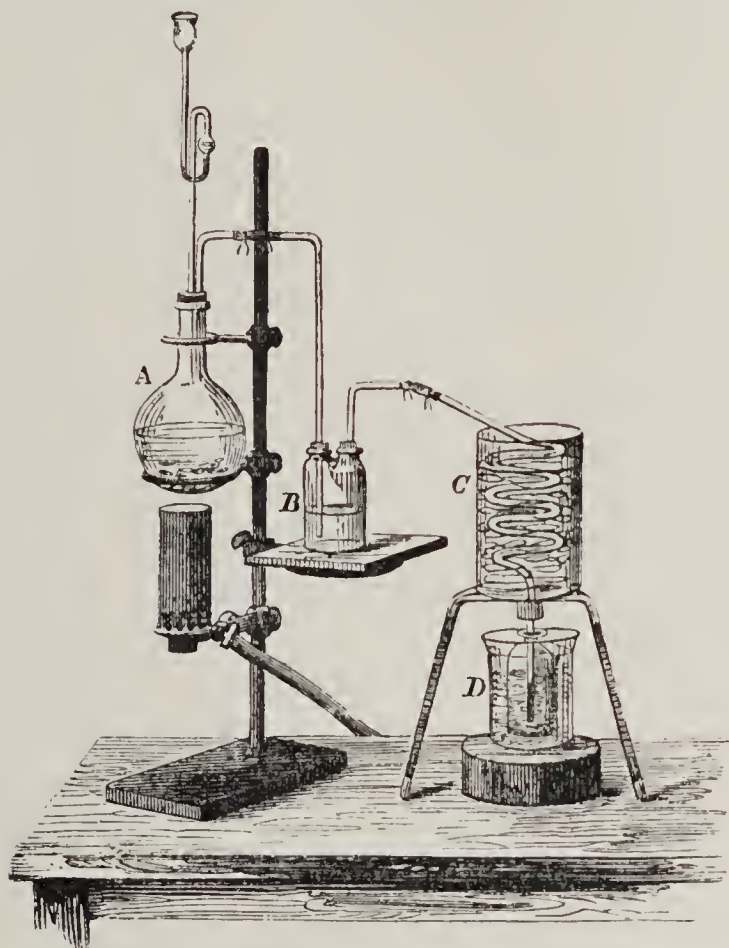


FIG. 65.

through the wash-bottle B, containing strong sulphuric acid to dry it; it then flows through the thin glass spiral placed in the inverted bell-jar C. C contains a freezing mixture of ice and salt, or, better, ice and calcium chloride. The condensed liquid sulphur dioxide is collected in a vessel surrounded by a freezing mixture of ice and salt contained in D.

119. Faraday's Method.—

Faraday used the following simple means to obtain increased pressure :

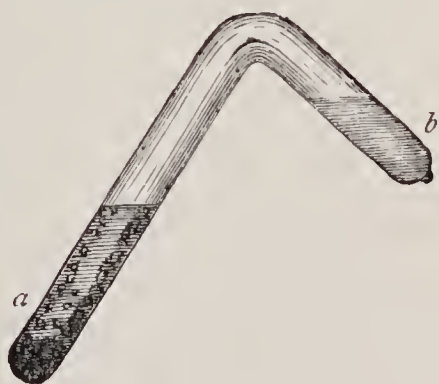


FIG. 66.

In the longer limb *a* of a bent tube (Fig. 66) is placed a

substance which, either by heating or by some chemical action, will produce the gas to be experimented upon. The short limb is then sealed. On heating the longer limb the gas is generated, the pressure increases, and in many cases, by the increased pressure, liquefies, in the short limb. In some cases the short limb is placed in a freezing mixture. Usually the amount of liquid formed is small, and can be the better seen if *b* be drawn out some 3 or 4 inches, with a much smaller diameter. Care must be taken that the part drawn out is strong, and that, in closing, the part closed is properly thickened.

If chlorine gas be passed into water just above the freezing point, crystals of chlorine and water, called hydrate of chlorine, and containing 28·4 per cent. of chlorine, will be formed. These crystals are rapidly dried with blotting-paper, and placed in the limb *a*, which is then inserted in a freezing mixture. The limb *b* is drawn out and sealed. *b* is now placed in a freezing mixture, while *a* is surrounded with warm water. The hydrate decomposes, and forms two layers: the lower is liquid chlorine; the upper, water. The chlorine distils into *b*, and is liquefied by the increased pressure.

Silver chloride readily absorbs many thousand times its volume of ammonia. Dry silver chloride (sufficient to nearly fill the limb) is placed in *a* before the end *a* is sealed. The ends *a* and *b* are drawn out ready for sealing. Dry ammonia is now passed through; it is absorbed by the chloride and it also drives out the air. Both ends are sealed. *b* is placed in a freezing mixture, and *a* is warmed gently with the Bunsen flame. The ammonia absorbed by the silver chloride is liberated, and the pressure is sufficient to condense it in *b* as colourless liquid ammonia.

The simple glass tube was not strong enough to resist high pressures; it was replaced by iron vessels, the pressure being obtained by the aid of force-pumps.

By such methods a large number of substances that had been regarded as permanent gases were liquefied, and proved to be vapours. But oxygen, nitrogen, hydrogen, carbon monoxide, and marsh-gas resisted all efforts, and were still spoken of as "the permanent gases."

The solution of the problem lay in the researches that follow.

120. Cagniard-Latour.—Cagniard-Latour used a curved tube closed at both ends (Fig. 67). *b* contained air above the mercury, and served as a pressure-gauge; *a* contained a small quantity of alcohol. Both ends were graduated, so that the volume of the liquid at any time was known. *a* was placed in a bath, and heated to any required temperature, and the following effects were noted: Part of the alcohol vaporized, but on increasing the temperature a point was reached where no distinction could be drawn between the liquid and its vapour; the volume at this point was about three times its original volume. The substance at this moment was at a temperature of about 250° C., and the pressure, indicated by *b*, was about 120 atmospheres.

Drion notices that the meniscus separating the liquid and its vapour, which at first was concave, gradually flattened as this point was reached, until it became a plane; then the plane of demarcation disappeared, the liquid and the vapour gradually approximated to the same condition, and the tube was filled with a vapour, the process of change having been gradual.

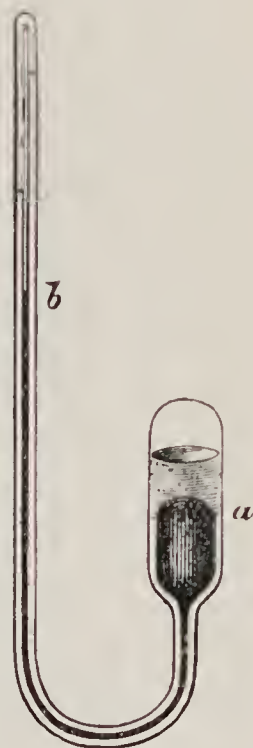


FIG. 67.

This suggests that at a sufficiently high temperature the difference between a liquid and a vapour no longer exists, and that the liquefaction of the gas must be sought for under this temperature. (Compare § 117.)

121. Andrews's Researches.—Dr. Andrews's researches set the matter in a clearer light. He experimented upon carbonic acid gas.

The gas was enclosed in a strong glass tube, *g*, and was shut in by a thread of mercury (Fig. 68). The tube was firmly set into a copper tube, *E R*, this latter being filled with water. The steel screw *S* worked into this tube; by turning it the required pressure could be obtained. The pressure was measured by

connecting the interior of R with a similar tube, in which was inserted a tube similar to *g*, but containing air. The second tube formed an air-manometer, and was previously graduated to measure pressures in atmospheres. The glass tube or tubes could be surrounded by a glass case containing water, which could be kept at any required temperature. Care was taken to compress slowly, and allow the gas to cool to the temperature required by the experiment.

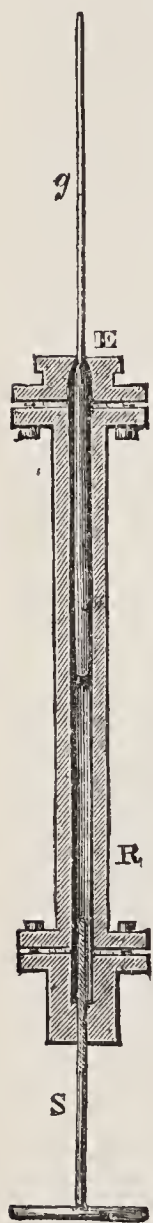


FIG. 68.

The results were graphically set out (Fig. 69), the ordinates representing pressure, and the abscissæ, volume.¹ The isothermals for various temperatures were drawn. Take the case when the temperature was 13.1° C. When the pressure is about 48 atmospheres, condensation begins, and the liquid and gas can be distinctly seen; the volume of the liquid after condensation is complete is about one-fifth of the volume of the gas before condensation; until condensation is completed there is no increase in pressure. Liquid carbonic acid being, compared with its gaseous form, very slightly compressible, little diminution of volume is shown as the pressure increases to about 90 atmospheres,—the isothermals are nearly vertical. (Compare this with the isothermal of steam, § 117.)

Now take the gas at a temperature of 21.5° C. Liquefaction only begins at 61 atmospheres. The volume of the liquid obtained when all is condensed is only one-third the volume of the gas before condensation.

There has been, in each of the previous experiments, a distinct break between the liquid and gaseous states. When the tube is at a temperature of 31.1° , the curve for some time suggests the isothermal line of a gas, and no condensation ensues. When the pressure is between 73 and 75 atmospheres, there is a flattening of the curve, suggestive of the flat part

¹ In Andrews's paper the ordinates represent volume and the abscissæ pressure. The dotted curve is also absent

of the 13.1° and 21.5° lines, but no physical difference can be detected in the gas. When the pressure increases

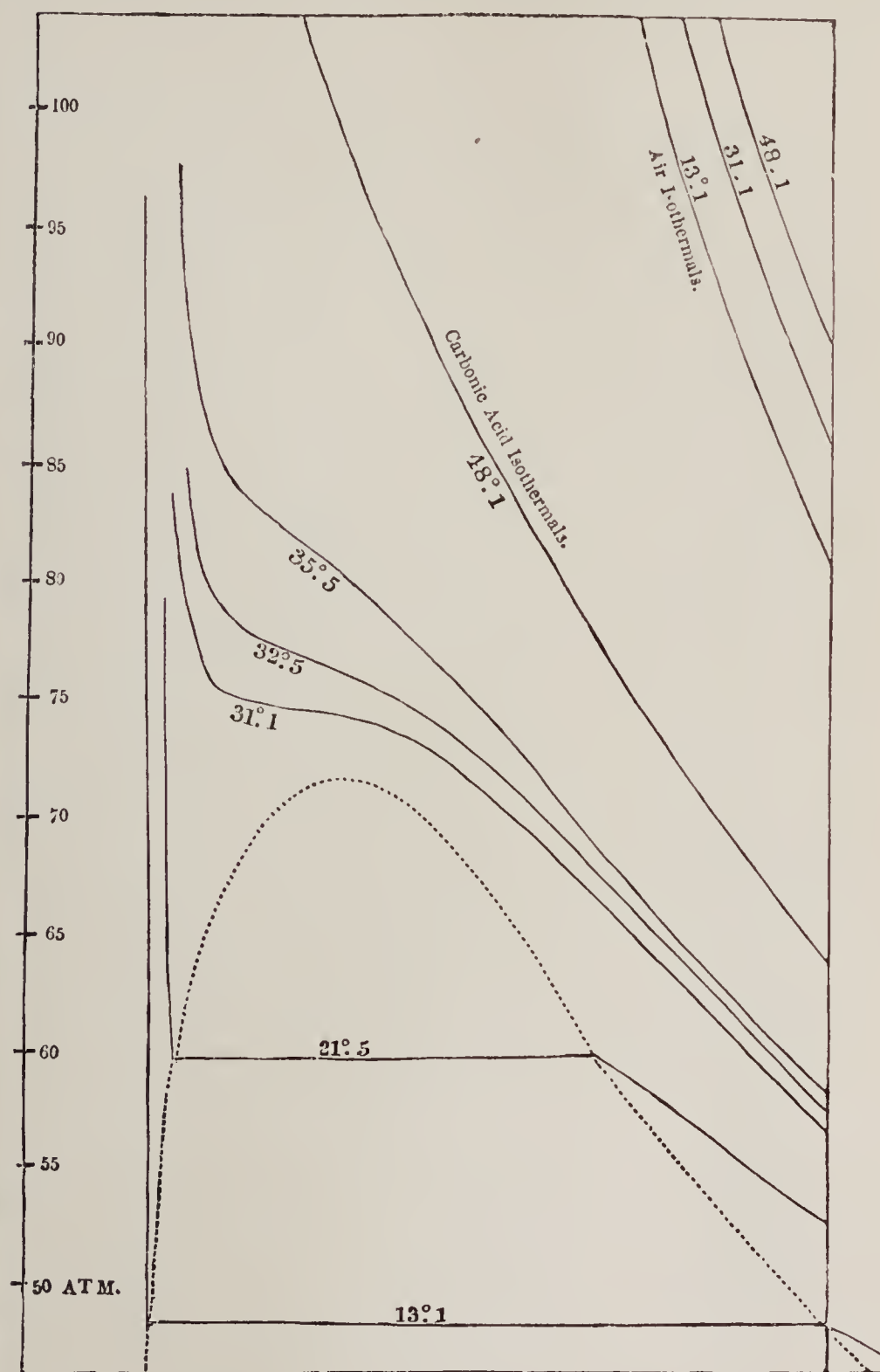


FIG. 69.

beyond 75, the diminution of volume continues, but at a much slower rate ; it is suggestive more of the diminution in volume

of a liquid. The same points are observable in the curves for 32.5° and 35.5° , but they disappear for 48.1° , when carbonic acid seems to be acting like a perfect gas, and obeys Boyle's law.

Dr. Andrews concluded that above a certain temperature the gas cannot exist as a liquid; this he determined to be 30.92° C. for carbon dioxide, and called it "the critical temperature." He states that other gases would, like carbonic acid, possess a critical temperature; in fact, carbonic acid gas, at a high temperature, behaves like one of the so-called permanent gases.

"The critical temperature of what are called the permanent gases is probably exceedingly low, so that we cannot by any known method produce a degree of cold sufficient, even when applied with enormous pressure, to condense them into the liquid state."

Since this sentence from Maxwell's "Heat" was written, it has been found possible to cool all the permanent gases, save hydrogen, below their critical temperatures.

The distinction between gas and vapour then disappears. A vapour is a gas below its critical temperature.

Referring again to Fig. 69, we see that for the critical temperature there is a certain pressure where condensation begins; it is somewhere about 75. This particular pressure is called "the critical pressure." When it is at the critical temperature and the critical pressure, unit mass has a definite volume, called "the critical volume."

122. Cailletet's Method.—

The apparatus (Fig. 70) is essentially like that of Dr. Andrews. The capillary tube T P contains the gas, cut off by mercury; the lower end of the tube is curved

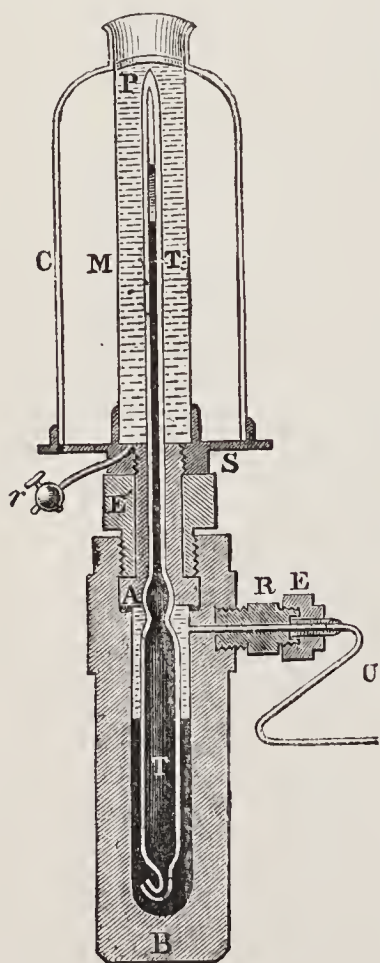


FIG. 70.

and open, and dips into a mercury bath, B. The tube is fitted into the bath by a screw, A. Pressure is transmitted from a hydraulic press, not shown, by means of the tube U passing through the screw R E. T P is surrounded by a bath, M, that contains a freezing mixture when necessary. The bath, in turn, is surrounded by a safety bell-jar, C.

Carbonic acid gas is by this apparatus easily liquefied at the ordinary temperature; but oxygen or nitric oxide, even when subjected to a pressure of 500 atmospheres, shows no signs of condensation. If after compression to between 200 and 300 atmospheres the heat be allowed to escape, so that the gas is again at the temperature of M, and the screw connected with the press be then suddenly opened, so that the pressure in T is instantly relieved, a mist suddenly appears and rapidly disappears; this must be due to the condensation of the special gas in the apparatus.

We have already seen that heat is required to expand gases. The gas expanding when the great pressure is relieved uses heat-energy, which is taken from itself. There is thus a sudden fall of temperature below the critical temperature of the gas, and the pressure yet remaining is sufficient to condense the gas. As soon as the pressure is further relieved, the liquid evaporates. By this apparatus oxygen, nitric oxide, and marsh-gas were liquefied.

123. Pictet's Method.—At the same period, and independently, Pictet liquefied these “permanent” gases by a different method. He obtained his pressure following Faraday's method; that is, he heated in a closed tube some solid or compound that would generate the gas required. For oxygen he used potassium chlorate.

The substances are passed into the iron retort L through P, which is then securely closed. The gas generated in L—the heat of the lamp O being used if necessary—collects in M (Fig. 71); the increase in pressure is indicated by the manometer R. The tube M is surrounded by a freezing mixture contained in H, that produces a temperature below the critical point of oxygen.

This low temperature is produced as follows: The condenser K is surrounded by a cylinder, C, containing liquid

sulphur dioxide; on working the pumps A and B, the liquid is evaporated (following the arrows), and is forced into a condenser, D, where it is cooled by water and liquefied under a pressure of 3 atmospheres. It then passes by the tube *d* to the tube C. Thus the sulphur dioxide is restored as liquid sulphur dioxide, but at a lower temperature, -70°C .

Into K, surrounded by this low temperature, is forced carbonic acid gas; this gas at -70°C . liquefies and is forced

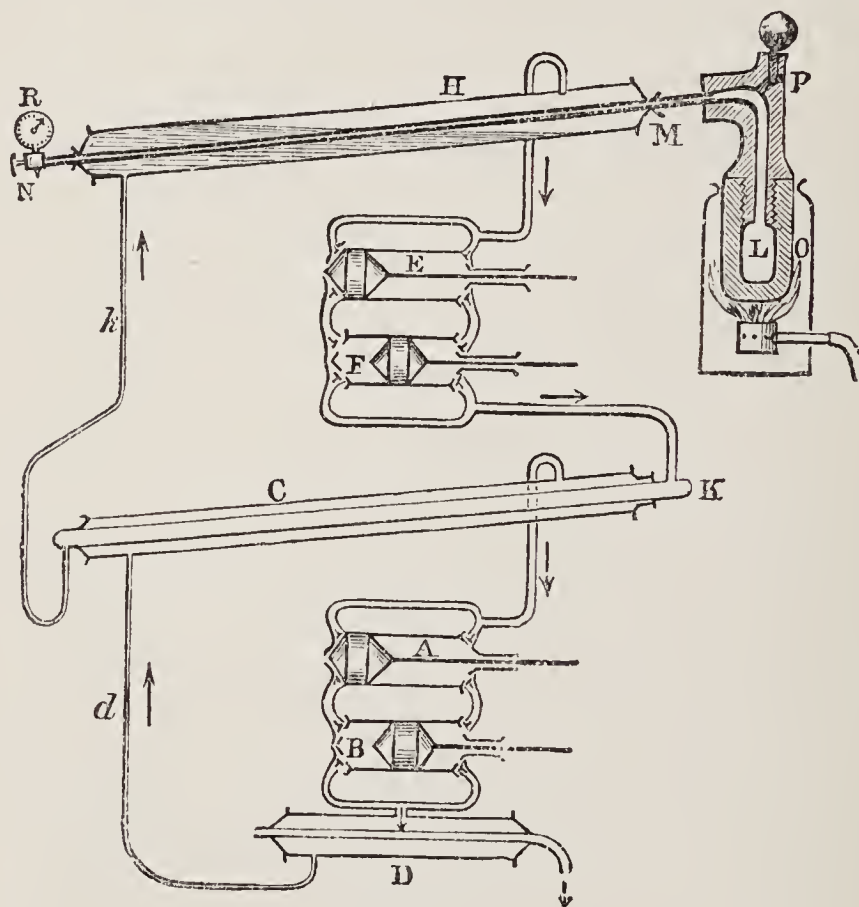


FIG 71.

into H, passing along *h*. The gas supply is now cut off, and, by working the pumps E and F, the liquid carbonic acid is evaporated so rapidly that it freezes, and its temperature sinks to -130°C . At this temperature, in the case of oxygen, when the manometer R indicates a pressure of 500 atmospheres, it suddenly sinks to 300 atmospheres, showing that part of the oxygen has condensed. On opening the stop-cock N the liquid issues as a white (?) jet and immediately evaporates. (See Dewar's description.)

Wroblewski and Olzewski modified Cailletet's apparatus

to produce yet lower temperatures. The tube containing the gas was bent twice at right angles (compare T, Fig. 70), and the end dipped into a vessel containing also a hydrogen thermometer. The vessel, otherwise closed, could readily be connected with a powerful pump to evaporate any liquid in it. Liquid ethylene flowed from a reservoir through a spiral surrounded by a mixture of solid carbonic acid and ether, and entered the vessel at a temperature of about -100° C. The ethylene was evaporated, and the temperature fell to -136° .

At this temperature oxygen liquefies under a pressure of only 20 atmospheres. By using liquid oxygen instead of ethylene, and evaporating, a temperature of -200° is reached. Vessels containing air or nitrogen at a pressure of 100 atmospheres are prolonged by a tube of glass that is placed in the liquid. If the pressure be relieved, they at once liquefy and remain liquid. The connection with the vessel is broken, and on opening them to the air they evaporate, and the temperature rises to -192° C. for air and -194° for nitrogen.

Dewar, by improved methods, has recently been able to obtain liquid oxygen in comparatively large quantities. It is of a beautiful sky-blue colour, possesses marked magnetic properties, and a characteristic spectrum; it boils at -182° C. under ordinary atmospheric pressure, and therefore rapid ebullition takes place when it is exposed to the air. He has shown that, when the vessel containing the liquid is placed in a glass receiver, and a vacuum more perfect than any hitherto attained is formed by condensing the mercury vapour in a Torricellian vacuum (the vacuum at -80° C. was about 0.000000003 of an atmosphere), the convection of heat when the residual vapour is kept still is greatly reduced; the evaporation of the liquid is so far lessened that it is possible to carefully examine the physical properties of liquid oxygen.

By evaporating liquid oxygen in a suitable receiver (compare § 100), a temperature is reached where air is readily liquefied; by a similar evaporation of liquid air, a yet lower temperature is obtained, approaching the critical temperature of hydrogen, which gas will probably soon be liquefied. Air liquefies, as a whole, as a murky blue liquid, but in boiling it

follows the laws of mixed liquids; nitrogen distils first, then a mixture of nitrogen and oxygen, and ultimately almost pure oxygen. At very low temperatures liquid oxygen becomes inert and loses its ordinary oxidizing properties; potassium, for example, that tarnishes at once in air, and combines with such energy with the oxygen of water that it is ignited, floats unaltered in cooled liquid oxygen. At very low temperatures the molecular motion is so far reduced that the properties of matter, as at present understood, seem to change.

	Boiling points (1 atmosphere pressure). Degrees Centigrade.		Critical temperatures. Degrees Centigrade.		Critical pressures. Atmospheres.	
Nitrogen	...	-194°	...	-146°	...	35
Oxygen	...	-182°	...	-112°	...	50
Ethylene	...	-136°	...	+9.2°	...	58
Carbon dioxide		-80°	...	31.9°	...	77
Ammonia	...	-39°	...	130°	...	115
Chlorine	...	-34°	...	141°	...	84
Sulphur dioxide		-10°	...	155°	...	79
Ether	+35°	...	195°	...	40
Alcohol	...	78°	...	235°	...	67
Water	100°	...	365°	...	200

124. Spheroidal State.—If a bright metal plate be heated to a sufficiently high temperature, and drops of water be allowed to fall on it, the water does not rapidly evaporate, but forms globules that roll and spin about. The water passes into the spheroidal state. The evaporation is very slow, and the state depends upon the plate being retained at a high temperature. If the lamp be removed, and the plate cools down, a point is reached when the globule boils rapidly away. The metal, for water, should be above 150° C.; for alcohol, 130°; and ether, 60°.

Measurements have shown that the globule is always below the boiling point of the liquid. Thus water was found to be at 95° C.; ether, 34°; liquid sulphur dioxide, -11°.

This leads to a remarkable result. If a platinum vessel be heated to redness, and liquid sulphurous acid be poured into it, the acid assumes the spheroidal state, and therefore its temperature is below -11°. Drops of water let fall into the acid are at once frozen.

Faraday mixed solid carbonic acid with ether, dropped it into a red-hot capsule, when it assumed the spheroidal state; the temperature was below -100°C . He now dropped mercury into the spheroid, when it at once solidified.

The spheroid does not touch the metal—a fact readily shown by experimenting on a level plate. A lighted candle can be seen on looking between the plate and the drop (Fig. 72).

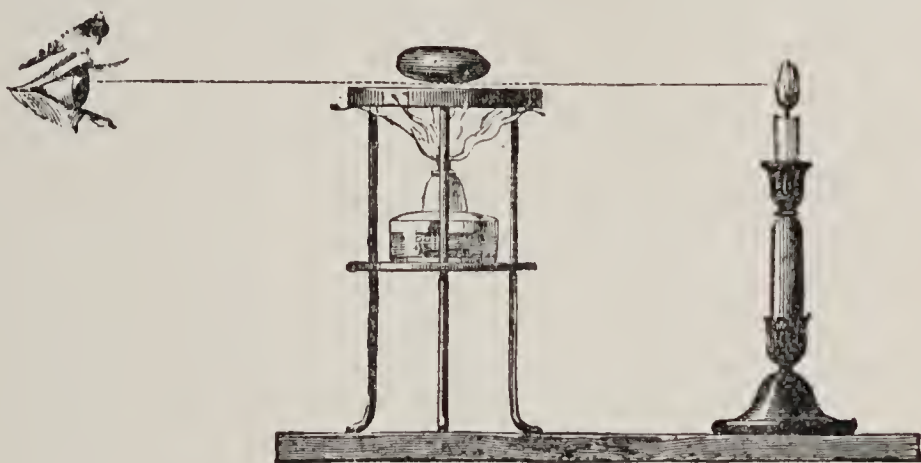


FIG. 72.

This is also demonstrated by connecting one pole of a battery (with a galvanometer in circuit) with the plate, and dipping the other pole into the spheroid. The absence of movement of the galvanometer needle shows that the spheroid and metal do not touch; it rests upon a cushion of its own vapour, that is continually renewed, and which transmits heat slowly, and therefore the only heat that reaches it does so by radiation.

The fact that the liquid does not touch the solid is also shown by heating a ball of copper to redness, and lowering it into a vase of water at about 99°C . An envelope of vapour surrounds the metal until its temperature falls to 140° , when contact takes place, and the water boils suddenly.

If the hand be cooled down by dipping it into ether, and then be dipped into hot lead, the cushion of ether vapour prevents harm taking place, provided that it be not kept long enough for the vapour to evaporate. By damping the hand with water, it can be dipped with safety into molten shellac.

125. Vapour-Density.—The process of finding the vapour-density of a substance will illustrate many parts of the preceding chapter.

The density of air has already been determined (see § 51) as 0.001293 gram; this is the mass of 1 c.c. at 0° C. and at 760 mm. pressure. The density of hydrogen is 0.0000896. As the mass of 1 c.c. of water under like conditions is 1 gram, the above numbers express the relative density of the substance to water.

For many purposes in chemistry and physics it is necessary to know the density of the vapour of a liquid or solid. The density is, as a rule, compared with the density of air or hydrogen under like conditions, and is a relative density.

The principle is (*a*) to volatilize a known mass of the solid or liquid, and measure the volume of the vapour produced under the conditions of temperature and pressure; or (*b*) to measure the volume of a certain vapour, and then determine its mass under the observed conditions of temperature and pressure.

If the volume of air be v , the temperature t , and the pressure p , then, by Boyle's and Charles's laws, the mass of v c.c. = $w =$

$$v(0.001293) \frac{p}{(1 + \alpha t)760}. \quad \text{1 litre of dry air at } 20^\circ \text{ C. and a}$$

pressure of 4 atmospheres, weighs $\frac{1000(0.001293) \times 4 \times 760}{(1 + 0.003665 \times 20)760}$

$$= \frac{5.172}{1.0733} = 4.818 \text{ grams.}$$

126. Hoffmann's Method.—Hoffmann's is a modification of Gay Lussac's method. A graduated tube, b (Fig. 73), called a eudiometer, about 40 inches long, is filled with mercury and inverted in a trough of mercury, g , the Torricellian vacuum being formed above the mercury. The eudiometer is surrounded by another tube, a . The liquid or solid to be vaporized is contained in a very small stoppered bottle, h (drawn on a larger scale). By weighing the bottle empty and again containing the liquid, the mass, m , of the substance is known. The stoppered bottle, placed under the tube in g , rises to f into the vacuum. A liquid, whose boiling point is known, is heated in e . The vapour enters the second tube by c , and escapes by d into a condenser. The increased temperature with diminished pressure is sufficient to vaporize the liquid. The advantage of the Torricellian vacuum is that,

being under reduced pressure, the boiling point is lowered (§ 100), and thus the experiment can be conducted at a much lower temperature than would be possible at ordinary atmospheric pressure.

Water boiled in *e* gives a temperature in *a* nearly at 100°C ., and this is sufficient to vaporize substances whose boiling point is 150° under ordinary atmospheric pressure.

The following readings are taken:—

(1) The temperature of the tube (*t*); that is, the boiling point of the liquid in *e*.

(2) The height (*h*) of *f* above the level of the mercury in *g*. If the barometer be *H*, then $H - h$ is the pressure to which the gas is subjected.

(3) The volume (*v*) of vapour formed in cubic centimetres, read from the tube.

Then a volume, *v*, of a substance, at a temperature t° and pressure $H - h$, weighs *m* grams.

1 c.c. of air at 0° and 760 mm. pressure weighs 0.001293 gram;
 \therefore 1 c.c. of air at t° and $(H - h)$ mm. pressure weighs

$$0.001293 \cdot \frac{H - h}{760} \cdot \frac{1}{1 + at} \text{ grams}$$

\therefore vapour-density of substance

$$= \frac{\text{mass of vapour}}{\text{mass of equal volume of air under like conditions}}$$

$$= m \div 0.001293 \cdot \frac{H - h}{760} \cdot \frac{1}{1 + at}$$

$$= \frac{m(1 + at)760}{0.001293(H - h)}$$

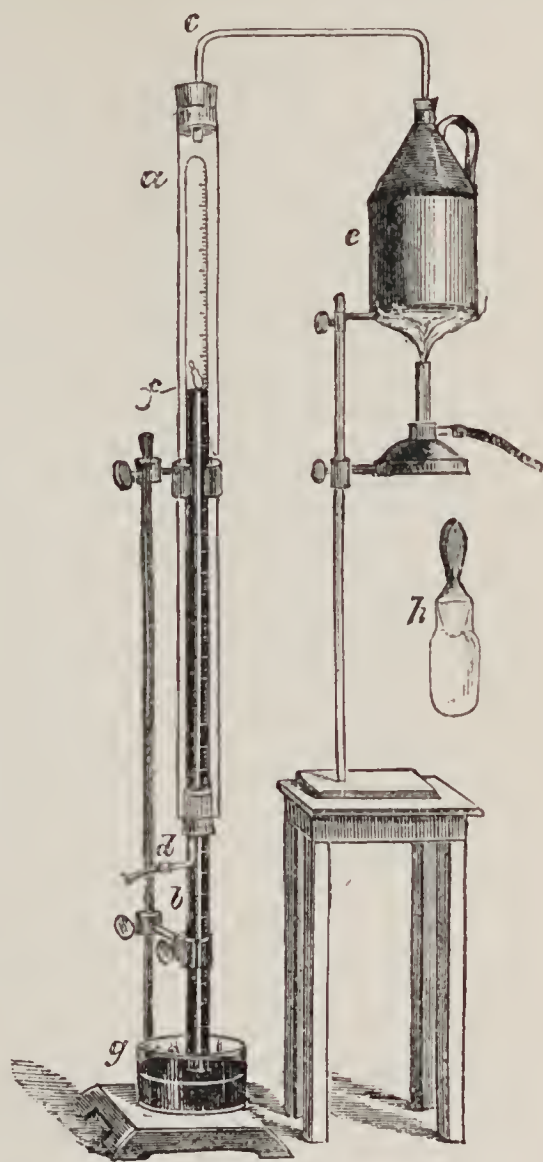


FIG. 73.

Example.—Find the density of chloroform vapour (air = 1) from the following data :—

Quantity of chloroform taken	= 0.096 gram
Volume occupied in tube	= 60 c.c.
Temperature of vapour	= 30° C.
Barometric pressure reduced to 0° C.	= 752 mm.
Height of mercury column in tube	= 506.7 mm.

(1) Substituting in formula, we obtain—

$$\text{Vapour-density} = \frac{0.096(1 + 0.003665 \times 30)760}{60 \times 0.001293(752 - 506.7)} = 4.26$$

Or (2) 60 c.c. of dry air at 30° C. and 245.3 mm. pressure weigh $\frac{60 \times (0.001293) \times 245.3}{760 \times (1.10995)} = 0.02256$ gram.

$$\therefore \text{vapour-density} = \frac{\text{mass of vapour}}{\text{mass of equal volume of air}} = \frac{0.096}{0.02256} = 4.26$$

Corrections.—(a) The height of the mercury column in the tube should be reduced to 0° C.

$$506.7 \text{ mm. of mercury at } 30^\circ \text{ C.} = \frac{506.7}{1 + 0.000181 \times 30} = 504 \text{ at } 0^\circ \text{ C.}$$

\therefore with this correction, vapour-density = 4.21

(b) The volume 60 c.c. is read at 30° C.; if the tube is graduated at 0°, the true volume is $60 \times (1 + 0.000025 \times 30) = 60 \times (1 + 0.00075)$.

\therefore 4.21 should be divided by $(1 + 0.00075) = 4.21 - 0.0031$

This correction only affects the third place of decimals, and can be neglected.

(c) The mercury in the tube depressed by the pressure of mercury vapour at 30°; this equals 0.06 mm., again a quantity we can neglect. If the tube were heated to a temperature of 200° C.; the pressure would be 19.9 mm., in this case too great to be neglected.

Generally $v \times (1 + kt)$ is the real volume of the vapour; k = coefficient of expansion of glass. If the temperature be above 100°, we must allow for the pressure of mercury vapour,

1) h , also in exact experiments the mercury in the tube will be practically at temperature t° , and therefore the true value of h will be $\frac{h}{1 + bt} = h'$; b = coefficient of expansion of mercury. Therefore a more exact formula would be—

$$\text{Vapour-density} = \frac{m}{v(1 + kt)} \cdot \frac{1 + 0.003665t}{0.001293} \cdot \frac{760}{H - h' - l}$$

127. Victor Meyer's Method.—A glass tube, b (Fig. 74), with a bent connecting tube, a , is placed in a bath, c , which contains a substance whose boiling point is constant, and is much higher than the boiling point of the substance to be vaporized. The top is closed with a cork, d . The liquid in c is boiled constantly for some time; this is known when no more air issues from the end of a , which is placed under water (or mercury). A graduated tube is filled with water and inverted over a in g ; the stopper d is removed, and a small glass tube containing a weighed amount of the substance, whose mass is m , is dropped in (the bottom of b is protected with asbestos). The substance passes into vapour, and displaces an amount of air equal in volume to the vapour formed; this enters the graduated tube. This amount is a fraction of the volume of the tube b , and being generally heavier than air, diffusion does not act sufficiently in the time to affect the result.

When no more vapour issues, the graduated tube is moved with the usual precaution to a deep vessel of water, depressed until the level inside the tube is the same as that of the water outside; and the volume v at the temperature t° of the room and the height of the barometer (H) is read. The pressure of water vapour, h' , at t° must be considered, and is read from tables.

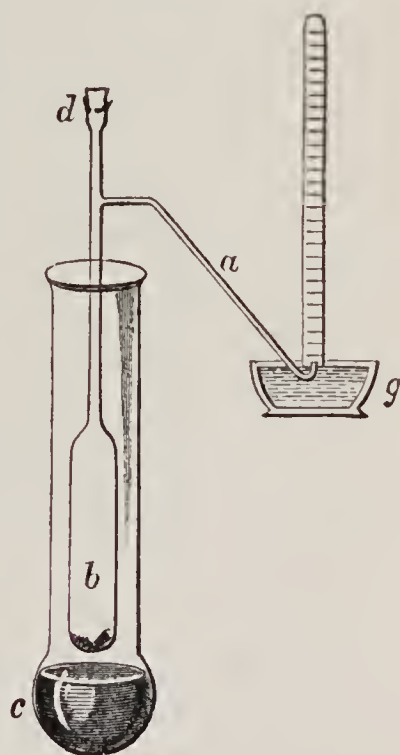


FIG. 74.

The weight of a volume, v , at t° and pressure $H - h'$, is m

$$\text{Weight of equal volume of air} = v(0.001293) \frac{H - h'}{760} \cdot \frac{1}{1 + at}$$

$$\therefore \text{vapour-density} = \frac{p \cdot 760(1 + at)}{v(0.001293)(H - h)}$$

If the vapour-density is to be calculated for hydrogen, we must take the weight of 1 c.c. of hydrogen at 0° and 760 mm.; this is 0.00008936 gram. The expansion for glass (the graduated tube) at low temperatures can be neglected.

The following is an actual example by Meyer's method, where the expansion of mercury in the barometer is allowed for—

(1) Weight of substance, 0.0355 gram.

(2) Volume of vapour in tube, 5.1 c.c.; temperature of room near tube when measured, 14°C .; barometer, 755.6 mm. at a temperature of 11.7°C .

(a) 755.6 mm. mercury at 11.7° reduced to 0° is 754.

(b) Gas in tube is subjected to a pressure of 754 mm. — the pressure of aqueous vapour at 14° ; this is 12 mm.

$$\therefore \text{pressure is } 754 - 12 = 742$$

Weight of 5.1 c.c. of hydrogen under like conditions

$$= \frac{5.1 \cdot 0.00008936 \cdot (754 - 12)}{760 \cdot (1 + 0.003665 \cdot 14)}$$

\therefore vapour-density of substance

$$= \frac{0.0355 \cdot 760 \cdot (1 + 0.003665 \times 14)}{5.1 \cdot 742 \cdot 0.00008936}$$

$$= 83.8 \quad (H = 1)$$

In practice the density of dry air has been determined, and the results tabulated for various temperatures and pressures; so that the value $\frac{0.001293(H - h)}{760(1 + at)} = \beta$ can be obtained at once, and the density is $\frac{m}{v\beta}$

Avogadro's law, that equal volumes of gases under similar conditions as to temperature, contain an equal number of molecules, is generally accepted. The determination of the

vapour-density, therefore, gives at once the molecular weight of a substance; *e.g.* hydrogen = 1, the following results are obtained:—

			Atomic weights.			Molecular weights.
Hydrogen	1	2
Oxygen	16	32
Water	9	18

accepting that a hydrogen molecule consists of 2 atoms, and that we represent its atomic weight by 1.

Then 2 is the molecular weight of hydrogen. If a given volume of hydrogen contains 2 units of mass, then an equal volume of oxygen under similar conditions weighs 32 units, and water vapour 18 units. We cannot determine the actual number of molecules in the volume, nor is it necessary; for let n be the number—

$$\frac{2}{n} = \text{mass of 1 molecule of hydrogen}$$

$$\frac{32}{n} = \text{,, 1 ,, oxygen}$$

$$\frac{18}{n} = \text{,, 1 ,, water vapour}$$

∴ the mass of—

$$\begin{aligned} 1 \text{ mol. of hydrogen} : 1 \text{ mol. of oxygen} : 1 \text{ mol. of water vapour} \\ :: 2 : 32 : 18 \end{aligned}$$

If from other considerations we know that 1 molecule of oxygen contains 2 atoms, then the atomic weight of oxygen will be 16.

EXAMPLES. VIII.

1. What is meant by “saturated” and “unsaturated” vapour?
2. How would you proceed to graph the isothermal for sulphur dioxide at the temperature of the room? Compare its isothermal with that of air.
3. Compare the molecular condition of 1 lb. of water at 100° with 1 lb. at 200° C.
4. Describe Andrews’s research in reference to the critical temperature of carbonic acid. Explain carefully “critical temperature,” “critical pressure,” and “critical volume.”

5. Explain the principle of Faraday's method of liquefying gases. Why is it impossible by such method to liquefy oxygen?

6. Describe Cailletet's and Pictet's methods of liquefying gases. Compare the principles of the two methods.

7. What meanings do you attach to "gas" and "vapour"?

8. To change water at 100°C. , under ordinary conditions, to steam at 100° takes a large number of thermal units, and time is necessary to give these thermal units to the water; if the steam passes into water, there is a sudden liberation of heat: how do you account for the phenomenon, in the liquefaction of carbon dioxide by Andrews's or Cailletet's method, that a slight change in temperature or pressure produces a change of state, and this marked liberation of heat does not seem to take place?

9. How can solid carbonic acid be made? Describe its appearance, and its use in producing freezing mixtures.

10. What is meant by the spheroidal state of water? How is it produced? Explain the phenomenon.

11. Explain "density." How have the densities of air and hydrogen been determined?

12. Calculate the vapour-density of a substance from the following data, obtained by Hoffmann's method (air = 1):—

Weight of substance	= 0.25 gram
Volume of vapour	= 35 c.c.
Temperature of vapour	= 100°C.
Corrected barometer in room	= 750 mm.
Height of mercury in tube	= 400 mm.

(1) Obtain an approximate result, and state exactly what corrections you neglect. (2) Apply corrections necessary to give a correct result to two places of decimals.

13. Calculate the vapour-density of a substance, from the following results obtained by Meyer's method:—

Weight of substance	= 0.15 gram.
Volume of air collected	= 30 c.c.
Corrected height of barometer	= 756 mm.
Temperature of room	= 20°C.

CHAPTER IX.

HYGROMETRY.

128. Moisture in the Air.—The presence of water vapour in the atmosphere at any time is shown—

(1) By exposing chemical substances that readily absorb moisture, such as calcium chloride, potassium hydrate, freely to the air. These salts absorb moisture, and ultimately dissolve in the water abstracted from the air. Strong sulphuric acid will also act as a hygroscopic substance. Or—

(2) By the visible condensation of the vapour on bodies whose temperature is sufficiently lowered. If a glass carefully rubbed dry on the outside be filled with cold spring water outside a room, moisture is generally deposited on the outside of the glass when it is brought into the room. Placing ice in such a glass makes the experiment more decisive. Even in winter, when the temperature is below freezing point, the presence of moisture can be shown by placing in the glass a mixture of ice and salt. The moisture will then freeze and be deposited as hoar-frost. In experimenting with Wollaston's cryophorus (§ 111), at first moisture is deposited; the moisture ultimately freezes.

The expressions in every-day use, "dry air," "moist air," "a dry day," simply express the effect of the air on ourselves and surrounding objects. They give no information as to the exact amount of moisture in the air; for example, a cubic foot of "dry air" in the tropics contains more moisture than a similar volume of air in England, and there is generally more moisture in the air in summer than in winter.

If the temperature of the air be sufficiently lowered, we have seen that, at a particular temperature, condensation of aqueous vapour takes place ; the air at this temperature is saturated.

The temperature at which the air is saturated with aqueous vapour, that is, the temperature at which condensation begins, is called the dew-point.

When the temperature of the air is greatly above its dew-point, we call the air dry ; this occurs both in summer and winter. The dryness generally consequent upon a cold east wind is a too familiar experience. If the temperature is near the dew-point, the air is “ damp.”

129. Hygrosopes.—For roughly showing the state of the atmosphere, hygrosopes are popularly used. Twisted catgut, when moistened, untwists and thus lengthens, shortening again when it dries. This explains the action of toys in which figures move out and in toy houses, according as the state of the air is far removed from or near the dew-point, and denote that rain is improbable or probable.

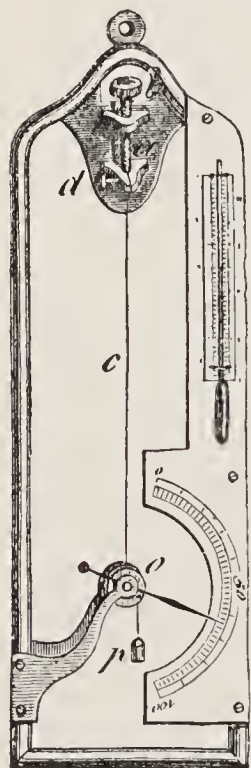


FIG. 75.

In Saussure's hygrometer (Fig. 75) a long human hair, *c*, cleaned by boiling it in carbonate of soda, is attached to a frame at *d*, passes over a pulley, *o*, and is kept stretched by a small weight, *p*. The hair contracts or expands according as the air becomes more or less damp, that is, according as the temperature is near to or far from the dew-point. Its movements are indicated by the index. Attempts have been made to graduate the scale, 0° denoting that the air is quite free from moisture, 100° that it is saturated. These attempts have not been so successful as to warrant its use as a scientific instrument. (See, however, § 134.)

Certain chemical salts, notably those of cobalt, change their colour according as they are dry or damp ; thus a toy figure dressed in garments dipped in such a salt and dried, is arrayed in blue on dry days and in pink on damp days.

130. Relative Humidity.—The problem in hygrometry is to measure the actual mass of aqueous vapour in a given volume of air at any time : this is the absolute humidity of the air. The maximum amount of vapour that the same volume of air could possibly contain under the same conditions of temperature and pressure, that is, the amount that would be present if the air were saturated, may be called the maximum humidity.

The ratio between the absolute and maximum humidity is called the relative humidity of the air. This is an important ratio in meteorology.

The atmosphere consists of the mixture of air and aqueous vapour, and the questions in hygrometry are simply applications of the knowledge possessed of the laws relative to the mixture of gases and vapours (§ 98).

The pressure of aqueous vapour at any temperature is the same, whether in a vacuum or in a space already filled by a gas. If air and aqueous vapour be mixed, the total pressure equals the pressure due to the air plus the pressure due to the vapour.

Under ordinary atmospheric conditions the pressure is never great, and it has been shown by experiments that the deviations from Boyle's law are so slight that they can be neglected. When the vapour is nearly saturated we should expect the deviation to be so great that it should be taken into account, but the experiments of Regnault and Herwig have shown that, up to the point of saturation of water vapour in air, Boyle's and Charles's laws can be applied without any marked inaccuracy.

The volume is generally measured in cubic metres, so that the mass of unit volume at 0° C. and 760 mm. pressure = 1293 grams.

$$\therefore \text{mass of 1 c.m. of air at } t^{\circ} \text{ and } p \text{ pressure} = \frac{1293 \cdot p}{(1 + at) \cdot 760} \text{ grms.}$$

Since air and the vapour within the limits obey the gaseous laws, the relation between their densities will be constant. It is found that the density of aqueous vapour is 0.622 times that

of air under similar conditions ($\frac{5}{8}$ is a convenient approximation).

$$\therefore \text{mass of 1 c.m. of aqueous vapour} = \frac{1293 \cdot p \cdot 0.622}{(1 + at) \cdot 760} \text{ grams}$$

Returning to our definition of relative humidity, we find that the problem is to calculate the relation of m , the mass of aqueous vapour actually present in a given volume (V , in cubic metres), when its pressure is p and temperature t° , to M , the mass of vapour the same volume of air could actually contain if it was saturated with aqueous vapour whose pressure would now be P .

$$\frac{m}{M} = \frac{\frac{V1293 \cdot p \cdot 0.622}{(1 + at) \cdot 760}}{\frac{V1293 \cdot P \cdot 0.622}{(1 + at) \cdot 760}} = \frac{p}{P}$$

That is, the masses are as the pressures of the vapour under the two conditions.

P is the maximum pressure taken from the tables, the result of experiments. p is difficult to determine directly, but is readily known from the following considerations: If we imagine a volume of air, V , separated from the rest of the atmosphere by an invisible film; and if P be the atmospheric pressure, and t the temperature; then by Boyle's and Charles's laws, for this mixture of air and vapour, $\frac{VP}{1 + at}$ is a constant. Seeing that during an experiment P does not change—

$$\frac{V}{1 + at} \text{ is a constant}$$

Now consider the aqueous vapour in this mixture. The volume, as before, is V , and its temperature t . Let the pressure be p , again $\frac{Vp}{1 + at} = \text{constant}$; but $\frac{V}{1 + at}$ is constant by above,

$$\therefore p \text{ is a constant}$$

It is therefore only necessary to determine p at a suitable temperature.

The method followed is to cool down the air until condensation just begins, and note the temperature of the dew-point. From tables the pressure at this particular temperature, and therefore at any other temperature, is known.

Hygrometry is then reduced to determining the dew-point.

131. Daniell's Hygrometer.—The bulbs A and B (Fig. 76), and tube connecting them, are simply Wollaston's cryophorus, save that ether is substituted for water, and that a delicate thermometer is inserted in the instrument, so that its bulb comes into the middle of A; B is surrounded with a piece of muslin. The ether inside is all run into A. Ether is then dropped on B; it rapidly evaporates; the temperature of B is lowered, and the ether vapour inside condenses; evaporation takes place from A, and reduces the temperature, the reduction being recorded by the thermometer. Soon moisture is deposited on the outside of A; that is, the dew-point (t) is reached. This will be lower than the actual dew-point. The dropping of ether on B is now stopped, and the temperature of A rises again. When the dew

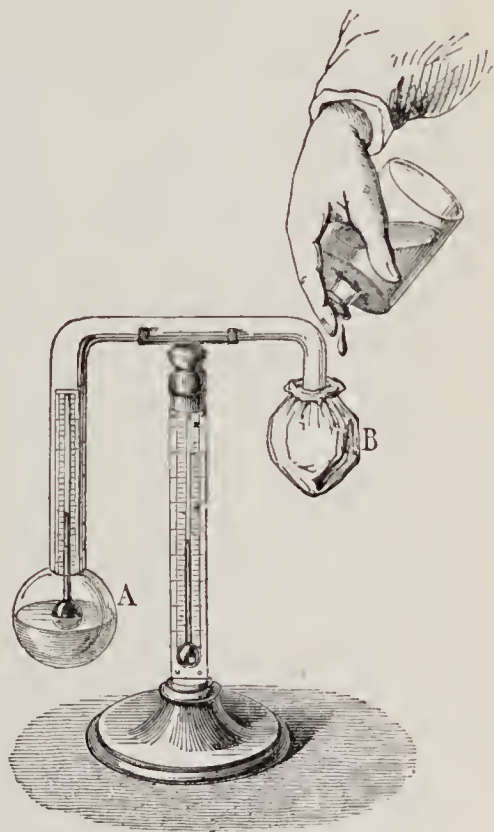


FIG. 76.

has disappeared, the temperature t' is read. The mean $\frac{t + t'}{2}$ is called the dew-point. To render the deposition more readily visible, A is made of black glass. It is an assistance in noting the point to draw a camel-hair brush across A; the streaks are readily seen. The temperature of the air is given by the thermometer on the stem.

The temperature of the room is 17.5° C.; the dew-point, as

read from a Daniell's hygrometer, is the mean of 14° C. and 14.5° C.: find the hygrometric state of the air.

$$\text{Dew-point} = \frac{14 + 14.5}{2} = 14.25^{\circ} \text{ C.}$$

The maximum pressure of aqueous vapour at $17.5^{\circ} = 14.88$

„ „ „ „ $14.25^{\circ} = 12.01$

$$\therefore \text{relative humidity} = \frac{m}{M} = \frac{p}{P} = \frac{12.01}{14.88} = 0.81$$

The instrument is not very reliable. It is not easy to exactly determine when the moisture appears and disappears. The evaporation of A is at the surface, and the thermometer dipping into the liquid may not give the exact temperature. Glass is a bad conductor, and the temperature of the outside is not therefore the same as that of the liquid. The observer also modifies by his presence the hygrometric state of the air. The evaporation of the ether from B, seeing it contains water vapour, also affects the result.

132. Dines's Hygrometer.—On turning a tap, B (Figs. 77 and 78), water flows from a vessel, C, along the pipe D.

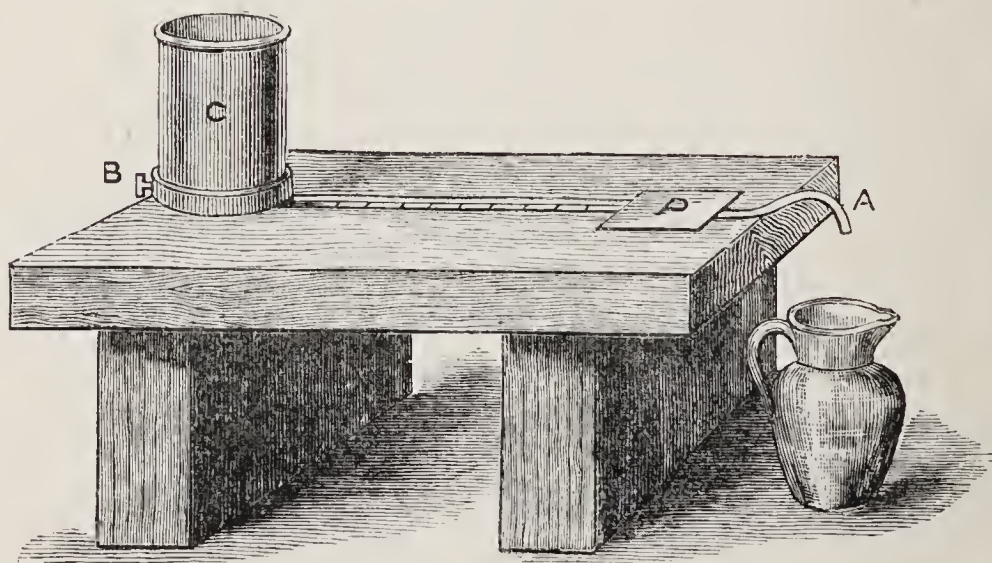


FIG. 77.

A diaphragm in the chamber R compels the water to flow round the diaphragm, pass over the top, and escape by the end pipe A (Figs. 78 and 79). Above the diaphragm, but not touching it, is the bulb of a delicate thermometer, T, graduated

horizontally. The chamber is closed above by a piece of very thin blackened glass, P, which is rubbed dry before any experiment. The water in C, cooled with ice if necessary, and kept well stirred, is allowed to run by turning B. As soon



SECTION

FIG. 78.

as dew is deposited on the blackened glass, the thermometer is read (t°). B is closed, and the thermometer read again (t_1°) when the film disappears. The mean, as before, is the dew-point. The experiment should be arranged so that the

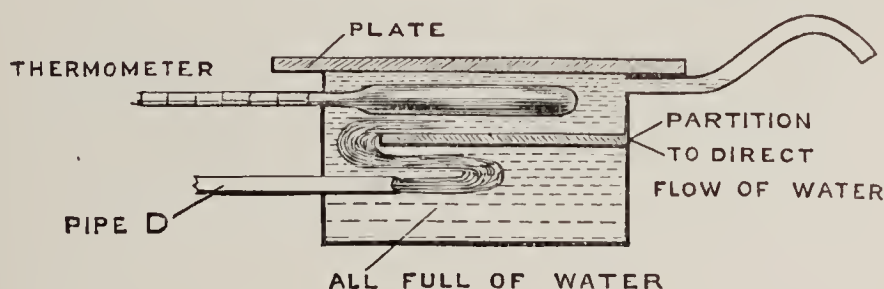


FIG. 79.

temperature of the water in A is not much below the dew-point. By care the temperatures t° and t_1° can be made to almost agree.

133. Regnault's Hygrometer—The glass tubes D, E (Fig. 80) are closed at the bottom by thin plain silver “thimbles.” A thermometer is inserted in each, T, t . D contains ether or alcohol, and is connected with a reservoir, G, by the indiarubber tube and the central system of the apparatus. G is filled with water. On allowing water to escape from G, air enters at A, bubbles through and evaporates the liquid in D. The consequent fall in temperature causes the deposition of dew, and the temperature of T is read. The tap is closed, and the temperature when dew disappears is

read. These two are brought as close as possible together, and the mean taken. E is not connected with D or G, and gives the temperature of the air at the time.

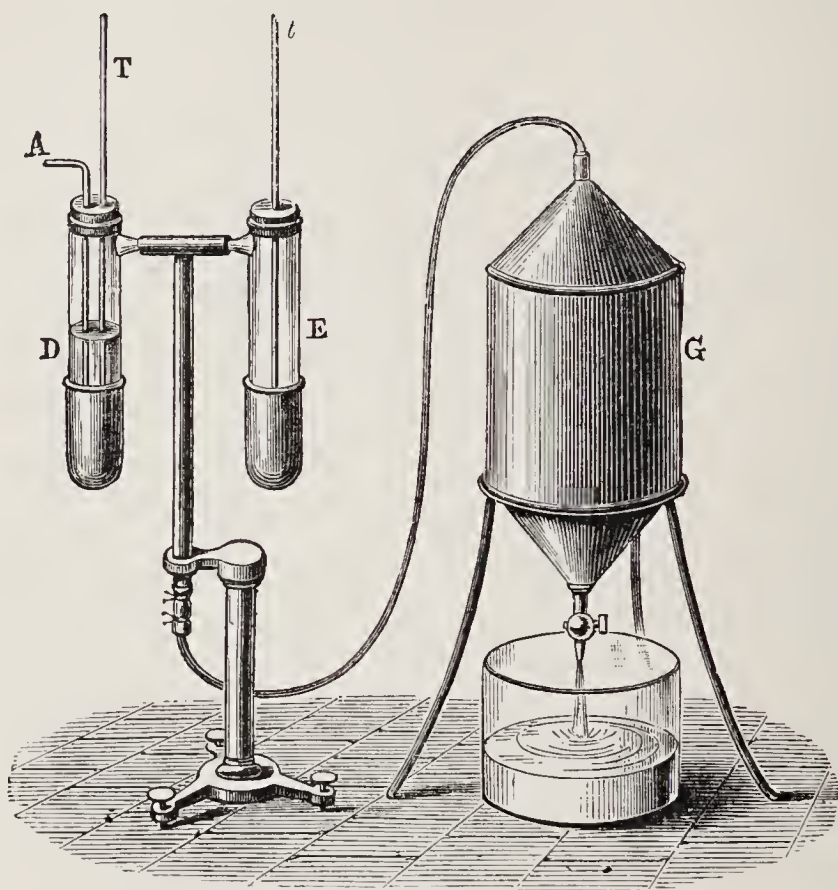


FIG. 80.

The hygrometer is readily imitated by using test-tubes (Fig. 81). The air is forced through by a pair of bellows. The vapour that escapes is condensed in a flask, which should be further removed from the apparatus than is shown in the figure, and kept in cold water.

134. The Wet and Dry Bulb Hygrometer.—In the instruments described, a distinct experiment has to be performed each time the dew-point is required; and, as we have seen, some trouble and care are needed to make a good determination. The advantage of the wet and dry bulb thermometer, first suggested by Leslie, and improved into its present form by Mason, is that the readings are always available (Fig. 82). It consists of two delicate thermometers hanging side by side. The bulb of one is surrounded with well-cleaned cotton, which

also dips into a reservoir of water ; this bulb is therefore always damp, and the evaporation from its surface lowers the temperature, so that its temperature, save when the air is saturated, is always below that indicated by the dry bulb ; and the

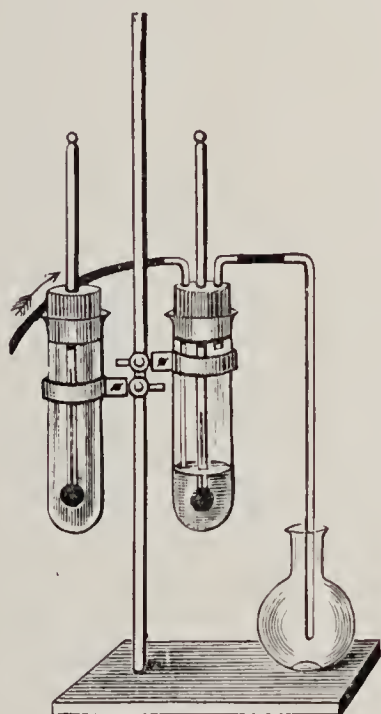


FIG. 81.

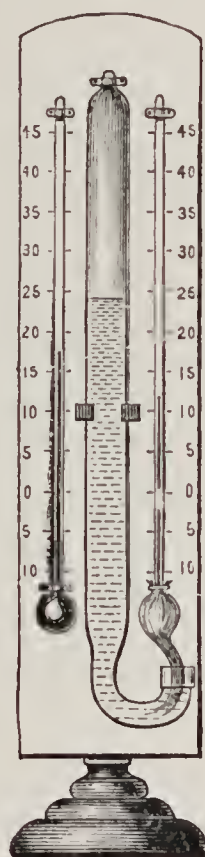


FIG. 82.

further removed the temperature of the air is from the dew-point, the greater will be the evaporation at the wet bulb, and consequently the lower will be its temperature.

Apjohn's formulæ, used in this country, are—

$$F = f - \frac{d}{87} \times \frac{h}{30}$$

$$F = f - \frac{d}{96} \times \frac{h}{30}$$

F is the pressure of the vapour in the air in inches ; f is the maximum pressure of aqueous vapour for the temperature of the wet bulb (taken from Regnault's tables) ; d is the difference between the readings of the wet and dry bulbs in degrees Fahrenheit ; h , the barometric height in inches. The value

87 is used above 32° F., and 96 when the bulb is surrounded with ice, *i.e.* below 32° F.

The sudden change of 87 to 96 in the denominator of the fraction at the freezing point suggests the uncertainty of the instrument at and near 32° F. In some countries the hair hygrometer (§ 129), carefully graduated, is used for observations near the freezing point.

h near the sea-level will not differ greatly from 30; therefore—

$$F = f - \frac{d}{87}$$

gives a useful approximation.

Practically, all meteorological results are recorded in England in degrees Fahrenheit and in inches. An approximate result, if the units used are degrees Centigrade and millimetres, is—

$$F = f - 0.00074hd$$

Having found F , the relative humidity is readily calculated. If we require the dew-point, it is only necessary to find the temperature in the tables opposite to the found value of F .

The results obtained from these formulæ have been checked over a long series of years with actual observations made with other hygrometers.

Glaisher has constructed a set of factors for finding the dew-point by inspection. For their use we have—

$$\delta = t_d - k(t_d - t_w)$$

δ is the dew-point; t_d is the temperature of the dry bulb; t_w is the temperature of the wet bulb; k is a factor depending upon the temperature of the dry bulb at the time of the observation.

GLAISHER'S FACTORS.

Dry bulb temperature.		Factor.	Dry bulb temperature.		Factor.
F.			F.		
30-31 $^{\circ}$...	4.1	45-50 $^{\circ}$...	2.1
31-32 $^{\circ}$...	3.7	50-55 $^{\circ}$...	2.0
32-33 $^{\circ}$...	3.3	55-60 $^{\circ}$...	1.9
33-34 $^{\circ}$...	3.0	60-65 $^{\circ}$...	1.8
34-35 $^{\circ}$...	2.8	65-70 $^{\circ}$...	1.8
35-40 $^{\circ}$...	2.5	70-80 $^{\circ}$...	1.7
40-45 $^{\circ}$...	2.2	80-85 $^{\circ}$...	1.6

Sets of tables based upon these factors and corrected from actual observations are also issued. A selection from these tables follows :—

Read- ing of dry thermo- meter.	Difference between dry and wet thermometers.									
	1°0'	2°0'	3°0'	4°0'	5°0'	6°0'	7°0'	8°0'	9°0'	10°0'
	Amount to be subtracted from the wet thermometer to obtain the dew-point.									
F.										
30°	3·2	6·3	9·5	12·6	15·8	18·9	22·1	25·2	28·4	31·5
31°	2·7	5·4	8·1	10·8	13·5	16·2	18·9	21·6	24·3	27·0
32°	2·3	4·6	7·0	9·3	11·6	13·9	16·2	18·6	20·9	23·2
33°	2·0	4·0	6·0	8·0	10·0	12·1	14·1	16·1	18·1	20·1
34°	1·8	3·5	5·3	7·1	8·9	10·6	12·4	14·2	15·9	17·7
55°	1·0	1·9	2·9	3·8	4·8	5·8	6·7	7·7	8·6	9·6
56°	0·9	1·9	2·8	3·8	4·7	5·6	6·6	7·5	8·5	9·4
57°	0·9	1·8	2·8	3·7	4·6	5·5	6·4	7·4	8·3	9·2
58°	0·9	1·8	2·7	3·6	4·5	5·4	6·3	7·2	8·2	9·0
59°	0·9	1·8	2·7	3·6	4·5	5·3	6·2	7·1	8·1	8·9
60°	0·9	1·8	2·6	3·5	4·4	5·3	6·2	7·0	7·9	8·8
61°	0·9	1·7	2·6	3·5	4·4	5·2	6·1	7·0	7·8	8·7
62°	0·9	1·7	2·6	3·4	4·3	5·2	6·0	6·9	7·7	8·6
63°	0·9	1·7	2·6	3·4	4·3	5·1	6·0	6·8	7·7	8·5
64°	0·8	1·7	2·5	3·3	4·2	5·0	5·8	6·6	7·5	8·3

The student will notice that the three methods for determining the dew-point do not give the same result. The theory cannot yet be said to be in a perfect state, and close agreement cannot therefore be expected.

135. Example.—The temperature of the dry bulb is 58° F., that of the wet bulb, 55° F.; the barometer stands at 29 inches: find the dew-point and the relative humidity.

The maximum pressure of aqueous vapour at 55° = 0·4329 inch; $d = 58 - 55 = 3°$; $h = 29$.

By Apjohn's formula—

$$F = f - \frac{d}{87} \times \frac{h}{30} = 0·4329 - \frac{3}{87} \times \frac{29}{30}$$

$$= 0·4329 - 0·0333 = 0·3996 \text{ inch}$$

From the tables the pressure of aqueous vapour at 52° is

0.3882; at 53° it is 0.4026; therefore the temperature of dew-point is $52\frac{11.4}{14}^\circ = 52.8^\circ \text{ F.}$

By Glaisher's formula we have—

$$\delta = t_a - k(t_a - t_w) = 58 - 3k$$

The factor for 55° is 1.9;

$$\therefore \text{dew-point} = 58 - 5.7 = 52.3^\circ \text{ F.}$$

From the tables we obtain at once, dew-point = $55 - 2.7 = 52.3$.

The maximum pressure at $58^\circ = 0.4822$ inch

$$\text{The relative humidity} = \frac{0.3996}{0.4822} = 0.83$$

136. Chemical Hygrometer.—The chemical method is also used for determining the relative humidity.

A known volume of air is drawn through drying-tubes containing hygroscopic substances, such as calcium chloride, pumice-stone dipped into strong sulphuric acid. The increase in the weight of the tubes (m) gives the amount of water vapour in a known volume of air at t° . The maximum amount can be calculated as before, M . Then—

$$\frac{m}{M} = \text{relative humidity}$$

137. Weight of Given Volume of Air or Gas.—To find the weight of a given volume of atmospheric air, let v be the volume in metres; P , the barometric pressure; t , the temperature; and t_1 , the dew-point. From the dew-point we can obtain the value p of the pressure of the aqueous vapour. By the law of the mixture of gases and vapour, we have—

(a) Weight of v metres of dry air at temperature t and pressure $P - p$. This

$$= \frac{v \times 1293(P - p)}{\left(1 + \frac{t}{273}\right)} \text{ grams}$$

(b) Weight of v metres of aqueous vapour at temperature t and pressure p = the weight of an equal volume of dry air multiplied by 0.622.

$$= \frac{v \times 1293 \times p}{\left(1 + \frac{t}{273}\right) 760} \times 0.622 \text{ grams}$$

$$\therefore \text{total weight} = a + b = \frac{v \times 1293 \times 273}{(273 + t) \times 760} (P - 0.378p) \text{ grams}$$

For example, when the barometric height is 762 mm., the temperature of the room 20° C., and the dew-point 16° C., find the weight of 10 cubic metres of air.

The pressure of aqueous vapour at 16° C. = 13.5 mm.

(a) The weight of 10 cubic metres of dry air at 20° C. and 762 - 13.5 = 748.5 mm. pressure

$$= \frac{10 \times 1293 \times 273 \times 748.5}{293 \times 760} \text{ grams}$$

$$= 11,865 \text{ grams}$$

(b) The weight of the aqueous vapour

$$= \frac{10 \times 1293 \times 273 \times 13.5}{293 \times 760} \times 0.622 = 113.1 \text{ grams}$$

$$\therefore \text{total weight} = 11,978 \text{ grams} = 11.978 \text{ kilograms}$$

$$\text{or total weight} = \frac{10 \times 1293 \times 273}{293 \times 760} (762 - 0.378 \times 13.5)$$

$$= \frac{10 \times 1293 \times 273}{293 \times 760} \times 756.897$$

$$= 11.978 \text{ kilograms}$$

Remembering that hygrometric state = $e = \frac{p}{P}$, if we know e , then for p we can substitute eP .

WORKED EXAMPLE.

1250 c.cm. of hydrogen are collected over water, the temperature of the water is 18° C., and the height of the water inside the collecting-jar is 10 cm. above the level of the water in the pneumatic trough: find the mass of dry hydrogen collected. The corrected barometer reads 756 mm.

(a) The maximum pressure of aqueous vapour at 18° C. = 15.36 mm.

(b) The density of water at 20° C. = 0.9983

„ mercury at 0° = 13.596

∴ a column of water 20 cm. high is equivalent to a column of mercury

$$\text{at } 0^{\circ} \text{ C.} = \frac{20 \times 0.9983}{13.596} \text{ cm.} = 1.47 \text{ cm.} = 14.7 \text{ mm. high}$$

(c) The total pressure inside the collecting-jar = $756 - 14.7 = 741.3 \text{ mm.}$

∴ the dry gas is subject to a pressure of $741.3 - 15.36 \text{ mm.} = 725.94 \text{ mm.}$

(d) 1250 c.cm. of hydrogen at 20° C. and 725.94 mm. pressure weighs

$$\frac{1.250 \times 0.0896 \times 273 \times 725.94}{293 \times 760} = 0.0997 \text{ gram.}$$

EXAMPLES. IX.

1. What is meant by the dew-point? How does the dew-point show the amount of vapour in the atmosphere?

2. Describe the action of Daniell's hygrometer. The temperature of the air is 18° C. , the dew-point is 12° C. : determine the hygrometric state of the atmosphere.

3. What is meant by the term "humidity," or "hygrometric state of the atmosphere"? The dew-point on a certain day is 12° C. , the temperature of the air being 16.5° C. : find its humidity.

4. Find the mass of 5 litres of air when the temperature is 15° , the dew-point 11.6° , and the barometric height is 758 mm.

5. What are the advantages of the wet and dry bulb hygrometer compared with a Daniell's hygrometer?

6. The air in a laboratory is 16° C. ; 5 c.cm. of air are drawn through a chemical hygrometer, and the drying-tubes show an increase of 50.4 grams: find the hygrometric state of the room, and the dew-point.

7. In an experiment 150 c.cm. of air are collected over mercury—the quantity is read after forcing up the tube sufficient water to form a thin layer—the barometer in the room reads 760 mm.; the thermometer, 25° C. ; the mercury in the tube is 300 mm. above the mercury in the trough: (1) find the mass of dry air; (2) determine its volume at 0° C. and 760 mm. pressure.

8. On Monday the dry bulb reads 60° F. , the wet bulb 52° F. , the barometer 758 mm. On Tuesday the dry bulb reads 58° F. , the wet bulb 53° F. , the barometer 761 mm. Using Apjohn's formulæ, compare the hygrometric states on the two days.

9. Describe Dines's hygrometer. Compare it with Regnault's and with the wet and dry bulb hygrometer.

CHAPTER X.

TRANSMISSION OF HEAT.

138. Convection.—In the experiments on ebullition (§ 99), particles of the liquid were heated, and, under the action of gravity, rose, heavier particles taking their place. Heat was in this experiment transferred from one part of the substance to another by convection. The convection currents are readily observable if a few pieces of bran or other light substance be thrown into the water.

Transference of heat by convection is the method followed in heating dwellings with hot water; it is seen on a large scale in the transference of heat by the Gulf Stream. Similar currents are observable in gases; the ascent of the heated particles of air above a lamp, the rise of heated air causing air-currents, are examples.

Convection currents may as readily be induced in fluids by cooling one part. In Fig. 83, if ice be placed in the test-tube, the water near it becomes denser, and sinks, and currents ensue. This illustrates the effect of the polar cold in causing ocean currents, their direction of flow being modified by the rotation of the earth and the shape of the land.

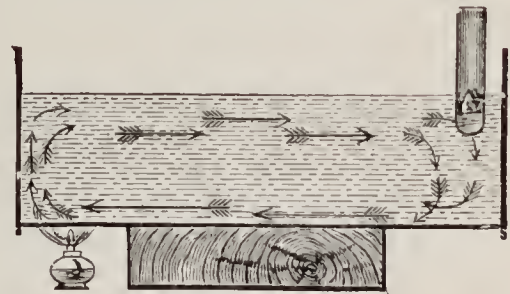


FIG. 83.

Convection of air is illustrated by ventilation and the draught of chimneys. The heating of the air reduces the density, and currents are induced.

139. Conduction of Heat.—When solids are heated, the heat is transferred from one point to another by conduction. The end of the poker placed in the fire rises in temperature, the near particles are heated, and so heat is ultimately transferred to the end. Metals generally are good conductors of heat, while felt, wool, etc., are examples of bad conductors.

We may roughly compare the conducting power of two solids, say iron and copper, by placing two similar rods end to end, and heating the junction. *After some time* we can try the furthest point from the junction where a match will ignite without friction. In an experiment the distance was 12 inches on the copper rod and 6 inches on the iron. Or

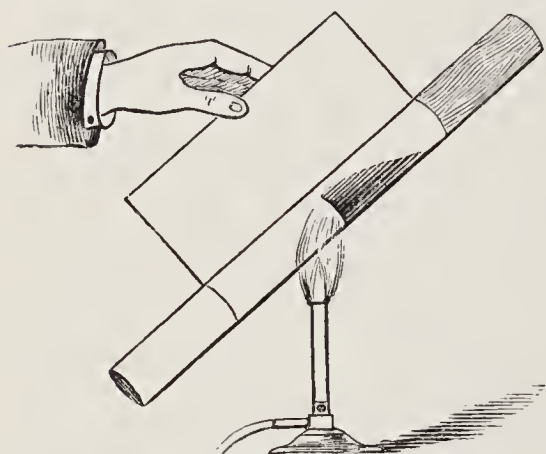


FIG. 84.

we may find the point where paraffin will just melt. Copper, we conclude, is a better conductor than iron.

A cylinder is made up (Fig. 84) of two cylinders, of wood and brass. Paper is tightly wrapped round it, and a flame is applied at the junction of wood and brass. The brass conducts away the heat

so rapidly that the paper is not scorched. Wood is a bad conductor, and the paper round it is at once burnt.

Liquids absorb heat readily; convection currents are also formed, so that fresh masses are brought under the influence of the heat. For this reason water can be readily boiled in egg-shells or cones made of paper; lead may be melted in a pill-box,—if a piece of paper, however, be dipped into the molten lead, it is at once charred.

The heat is conducted through the envelope to the water or lead; it is there used to raise the temperature; the water boils, as the temperature cannot rise above 100° C.; the heat is then utilized in evaporating the water. A slightly altered explanation applies to the lead.

Solids may be readily arranged in order of their power of conducting heat, by the following experiment:—

A number of similar small cylinders of same height and diameter are made of copper, brass, bismuth, wood, cork, etc. The simple air-thermometer is clamped (Fig. 85). One cylinder of copper is placed in boiling water for some time, and is used always in the experiment as the heater. Begin with the cylinder of lead, and place it on the top of the air-thermometer, then place above it the heater at 100°C. ; the heat is conducted through the lead, heats the air in the thermometer, and the liquid sinks. Wait until it reaches its lowest point, and note the position. Remove the copper to its bath, take away the lead, and wait until the liquid rises to its original position. Place now a second cylinder, say bismuth, on the top, and repeat the experiment. The greater the amount of heat conducted, the greater will be the expansion of the air, and the further will the liquid in the tube be depressed.

The following will be the order, beginning with the best conductor: (1) copper; (2) brass; (3) iron; (4) lead; (5) bismuth; (6) wood; (7) cork.



FIG. 85.

A little consideration will show that this rough experiment admits of many inaccuracies. The heat from the heater has first of all to raise the temperature of the cylinder experimented upon; this depends, not upon its power of conducting heat, but upon its capacity for heat. It is only after the substance ceases to rise in temperature that heat will be transmitted through it in a way that we can say is due to conduction. We have, in fact, to discriminate between rise of temperature and conduction of heat.

In all such experiments relative to conductivity we must see that the temperature of the substance is steady before we measure conductivity; that is, the flow of heat must be steady. The student will now see the force of the phrase, *after some time*, used in this section.

140. Ingenhaus's Apparatus is a metal trough with rods of various materials, but of the same diameter and length passing through corks in the side (Fig. 86). The rods project the same distance into the trough, and are coated outside with wax. Hot water is poured into the trough, and the

rate at which the melting of the wax travels along each rod is observed; this is evidently observing the rise of temperature.

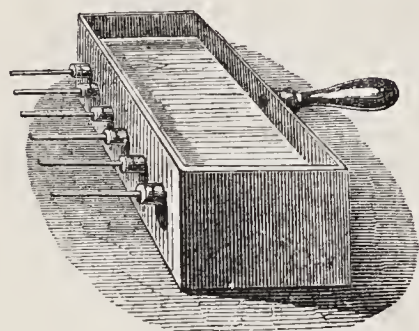


FIG. 86.

After the flow of heat is steady, the distance melted along each rod is measured. The greater the distance, the greater the conducting power of the solid.

141. Despretz's Method.—

Despretz formed the solids on which he experimented into similar long bars (Fig. 87), A, B; one end was turned and dipped into a bath of molten metal that gave a constant source of heat. Thermometers, t , t' , \dots , t'' , were inserted into small cavities in the bar, at equal distances apart; the cavities were filled up with mercury. A screen, S, protected the bar from the heat of the flame. Readings were taken when all the thermometers remained stationary. If the

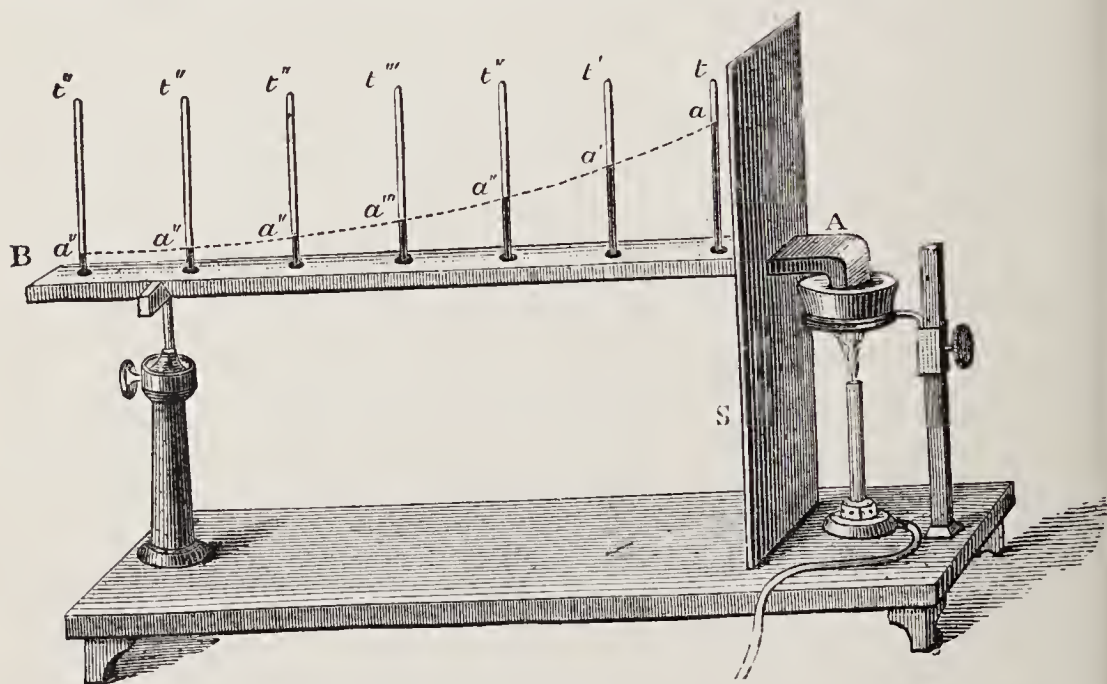


FIG. 87.

thermometers be of similar construction, and the tops of the columns of mercury be joined, a curve, a , a' , \dots , a'' , is formed.

The heat passing through any section, say a section near the thermometer t'' , is now a constant quantity, and t'' ceases

to rise, because the heat passing through the section is just sufficient to balance the heat lost in the bar from t'' to B by radiation and by convection (air-currents). By subtracting the general temperature of the room from the temperature indicated by each thermometer, we obtain the excess of temperature of each point above the rest of the room. Let us suppose the rod is divided into eight equal parts, then if we erect perpendiculars at each point, proportionate to the excess of temperature, we can plot out a curve that graphically shows the results of each experiment.

Despretz gave as the result of his experiment the law that, the distances along the rod being in arithmetical progression, the ordinates, measuring the excess of temperature, decrease in geometrical progression.

For example, if the distances of t, t' , etc., from A be 1, 2, 3, . . . 7 feet respectively, then the excesses of temperature above the room for each thermometer will be something like the following:—

Distance	1	2	3	4	5	6	7
Excess	100	70	49	34	23	16	11

where $\frac{70}{100} = \frac{49}{70} = \frac{34}{49}$, etc., $= \frac{7}{10}$ approximately.

This law does not admit of general application; it must be restricted to good conductors.

By such observations the relative conductivities of metals were determined.

142. Wiedemann and Franz's Method.—We have seen that the flow of heat must be steady; but as the experiments depend upon the radiation, the surface of the bars must be similar and equal in each experiment. This latter condition was attained by Wiedemann and Franz by making bars exactly equal in dimensions, and by electroplating the surfaces; they further improved the method by using small thin bars that admitted of greater care being taken with regard to their purity and condition as to annealing, etc. Instead of the high temperature (that of molten metal) at one end, as in the case of the previous experiments, it was found sufficient

to keep one end at 100° C. A small specially constructed thermo-pile (§ 152) was used to determine the temperature of the various points of the bars, thus avoiding the break in the continuity of the bars caused by the holes for the thermometers. The small bars were further placed in strong cylindrical glass vessels which were surrounded by water; the bars were therefore experimented upon in an enclosure whose conditions could be kept constant. The air in the glass vessel could also be exhausted, so that observations could be made *in vacuo*, eliminating thereby the effect of air-currents.

These two experimenters constructed a table of relative conductivities, taking the conductivity of silver, the best conducting metal, as 100.

TABLE.

Silver	...	100.0	Steel	11.6
Copper	...	73.6	Lead	8.5
Gold	...	53.2	Platinum	8.4
Brass	...	23.1	Rose's alloy	2.8
Tin	...	14.5	Bismuth	1.8
Iron	...	11.9				

The experimental work in connection with conductivity is difficult; slight impurities and differences in physical condition greatly affect the results. The following table, due to Gracet-Calvert and Johnson, will show this clearly:—

Relative conducting power. Silver = 1000.						
Silver	1000
Copper, rolled	845
Copper, cast	811
„	„	with 0.5 per cent. of arsenic	669
„	„	„ 1 „	„	„	...	570
Antimony, cast horizontally	215
„	„	vertically	192

143. Conductivity.—Such numbers are useful for comparison only. In order to give definiteness to the idea of conductivity, the following conditions are imagined: The

substance whose conductivity we wish to measure is supposed to be made into a plate, 1 centimetre thick and of unlimited area. The two sides are each kept at a constant temperature, one being 1° above the other. When the flow of heat is steady, the quantity of heat that passes through one square centimetre far removed from the edges of the plate of the substance in one second, measures the thermal conductivity of the substance.

The quantity of heat (Q) transmitted will vary (1) as the area of the surface (A); (2) as the time (t); (3) as the difference in the temperatures of the two faces (θ); and (4) it will vary inversely as the thickness (d). That is—

$$Q \propto \frac{At\theta}{d}; \text{ or, } Q = k \frac{At\theta}{d}$$

where k is a factor whose value will change for each substance.

With unit area (1 sq. cm.), unit time (1 sec.), unit thickness (1 cm.), and unit difference in temperature—

$$Q = k$$

Example.—How much water will be evaporated per hour when it is boiled at 100° in an iron boiler 1.5 cm. thick, having the area of the heating surface equal to 460 sq. cm., and its outer surface kept at 180° C., the conductivity of iron being 0.175 (Day's Examples)? (See § 149.)

$$\text{Quantity of heat} = Q = k \frac{At\theta}{d} = \frac{0.175 \times 460 \times 3600 \times 80}{1.5}$$

$$\therefore \text{mass evaporated} = \frac{Q}{537} = \frac{0.175 \times 460 \times 360 \times 80}{1.5 \times 537} = 28782 \text{ grms.}$$

Seeing that in such examples as the above all the quantities save k can be determined, it seems that some modification might be adopted for measuring k ; and this method has been followed by Peclet and others. It is found, however, in practice that such methods are unsuitable for exact determinations.

The change in the values of the coefficients of expansion, in the specific heat, etc., as the temperature changes, will suggest also that conductivity will vary with the temperature.

144. Forbes's Method.—The principle of the method used by Forbes is as follows:—

One end of a bar is kept at a permanent temperature, as in Fig. 87. Small holes are drilled at various distances along the bar, in which thermometers are inserted, the holes being then completely filled by a few drops of mercury. After several hours the temperature of each part of the bar, as indicated by the thermometers, is steady. The quantity of heat that passes any section (C) of the bar (Fig. 88)—whose temperature is

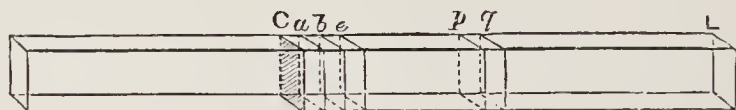


FIG 88.

known—is equal to the heat lost by radiation and the convection of air-currents by the part C L. This quantity is known if we can determine the quantity of heat lost by each of the lengths Ca, ab, bc, . . . pq, etc.; we have simply to add these quantities together.

In order to determine these quantities, a preliminary experiment is made by heating an exactly similar, but shorter, bar to a high temperature, inserting a thermometer, and allowing the bar to cool under similar conditions to those experienced by the experimental bar. The temperature of the bar is noted at certain intervals, frequently at first, and less frequently as the bar cools.

By this experiment we know the number of seconds, n , it takes the bar to cool from t° to t_1° .

$$\therefore \frac{t - t_1}{n} = r = \text{rate of fall of temperature}$$

And by taking t_1 as close as possible to t , we can determine the rate of fall of temperature at t° (see paragraph illustrating Figs. 89 and 90).

If s be the specific heat of the metal at that temperature, and m the mass of unit length—

Then smr = loss of heat per second per unit length at t°

From the data a table is constructed, and from it we can

at once determine the quantity of heat unit length of the bar will lose in unit time at any temperature within the limits of the experiment.

Then in the experiment we know the temperature of p and q (Fig. 88), and its length, and from the results obtained from the cooling of the short bar we can determine the amount of

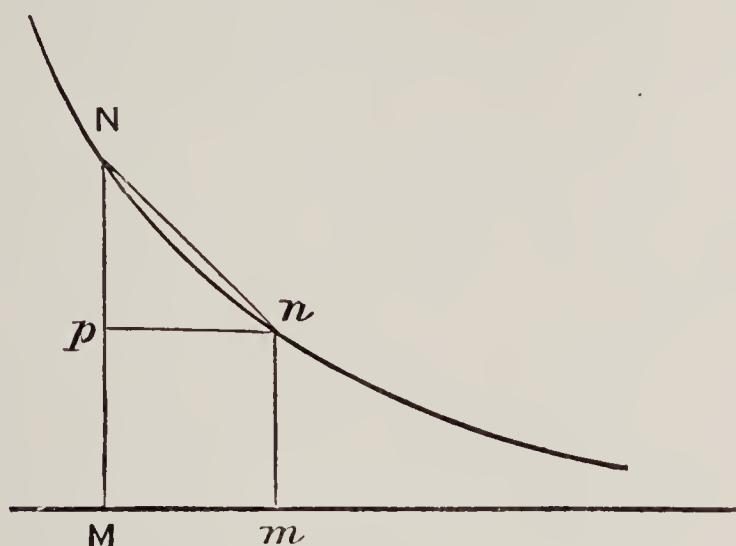


FIG. 89.

heat radiated. By calculating for every such distance, taking the distance as small as possible, and adding, we obtain the amount of heat that has passed the section C.

If MN (Fig. 89) represents the excess of temperature of the

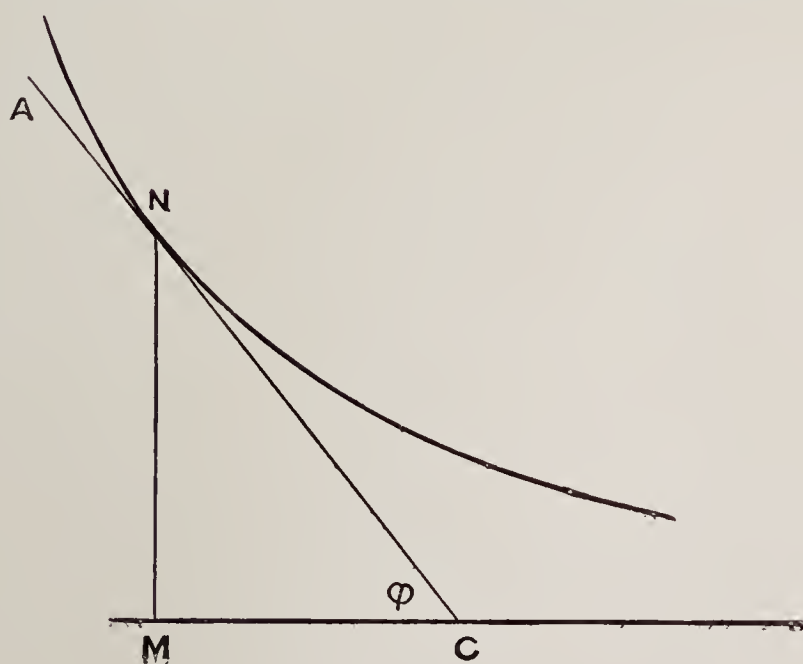


FIG 99.

thermometer at M above the temperature of the room, and mn the excess of the thermometer at m , then the temperature has fallen $MN - mn = \phi N$ for a distance Mm , and therefore the fall per unit of length is $\frac{\phi N}{Mm}$; that is, the tangent of the angle Nnp measures the rate at which the temperature is decreasing. If m be very near to M , the line joining Nn becomes AC , the tangent to the curve at N (Fig. 90). This tangent makes an angle ϕ with the bar.

$$Q = k \left(\frac{\text{difference of temperature}}{\text{thickness}} \right) At = k \tan \phi \times At$$

If we take A as unit of area, and t unit of time—

$$Q = k \tan \phi$$

(1) The curve can be constructed from experiments (see beginning of § 141);

$\therefore \phi$ is known for any temperature

(2) We have shown that Q can be determined by adding the amounts of heat radiated by each small portion of the bar;

$\therefore k$ can be determined for any given temperature

145. Thermometric Diffusivity.—In the definition given in § 143, the flow of heat is steady; that is, no part is used for raising the temperature of the bar. In making observations upon conductivity it is not always possible to have a steady condition of temperature in every part of the bar, and results have to be obtained from readings made when the temperature is rising or falling, as for example in the fall of the temperature of the small bar in Forbes's experiment. The change of temperature not only depends upon the conductivity, but also upon the capacity of the body for heat. Part of the heat only is transmitted from particle to particle; the remaining part is used in raising the temperature of the various parts of the bar. The greater the capacity of a substance for heat, the less will be the rise of temperature for a given supply of heat; the greater the conductivity, the greater will be the rise in temperature; that is, we measure a quantity (K) that varies directly

as the conductivity, and inversely as the thermal capacity, so that $K = \frac{k}{c}$. c , the thermal capacity of unit volume, equals the product of the density and the specific heat.

When the flow of heat is not steady, what is measured is the ratio of k to the thermal capacity; that is, $\frac{k}{c}$. This ratio is called "the coefficient of thermometric conductivity" by Maxwell; and "the coefficient of thermal diffusivity" by Thomson.

In determining K , we measure the effect that a quantity of heat in passing through unit volume of the substance produces on the temperature of this volume. It was this that lead Maxwell to give to $K = \frac{k}{c}$ the name "thermometric conductivity," giving the name "calorimetric conductivity" to k . Thomson gave the name "thermal diffusivity" from the analogy between the coefficient as defined and the coefficient that expresses the rate at which diffusion takes place between two liquids.

The student should carefully observe which coefficient is given in examples.

Forbes, by his experiments, found the conductivity of iron at various temperatures. He experimented upon two bars, one $1\frac{1}{4}$ inch square, the other 1 inch square. His units were foot, minute, and the heat required to raise one cubic foot of iron one degree C.

Temperature.	Thermometric conductivity or diffusivity $\frac{k}{c}$			
	1 $\frac{1}{4}$ -inch bar.		1-inch bar.	
0° C. ...	0.01337	...	0.00992	
50° C. ...	0.01144	...	0.00904	
100° C. ...	0.01012	...	0.00835	
200° C. ...	0.00876	...	0.00764	
275° C. ...	0.00801	...	0.00724	

Forbes noticed that the order of the metals, with respect to their thermal diffusivity, was the same as their order with respect to their electrical conductivity; his experiments on the iron bars showed that the thermal diffusivity decreased as

the temperature rose, analogous to the decrease in electrical conductivity following a rise in temperature. This suggested that the relation would be the case with all metals.

Having determined the thermal diffusivity, $K = \frac{k}{c}$, the absolute conductivity can be calculated by multiplying k by c . For example, the thermal diffusivity of a specimen of copper at 20° is 1.164.

$$c = \text{specific heat} \times \text{density} = 0.0933 \times 8.9 = 0.830$$

This would give the absolute conductivity as $1.164 \times 0.830 = 0.966$.

The units are the centimetre, gram, second.

Absolute conductivity.			Absolute conductivity.		
		k			k
Copper	...	1.108	Iron	...	0.164
Zinc	...	0.307	German silver...		0.109
Brass	...	0.302	Ice	...	0.0057

The tables give results without specifying the temperature. The temperature, however, as we have seen, slightly affects the results, especially in metals, and the result should probably be of the form $a(1 + bt)$.

There is considerable disparity in the results of different experimenters. This is markedly the case in the effect of temperature. Forbes gave the general result that the conductivity of all metals decreased with rise of temperature. Tait, experimenting with the same bar, found that all save iron increased in conductivity as the temperature rose; Mitchell, again, using the same bar, that the conductivity of iron, like other metals, increased with rise of temperature, and this seems to be the true law.

146. Dimensions of Conductivity.—The quantity of heat $Q = k \frac{At\theta}{d}$ (§ 143), substituting the dimensions of area, time, temperature, and thickness

$$[Q] = k \cdot \frac{L^2 T \Delta}{L} = k L T \Delta$$

The dimensions of conductivity will depend upon the units used in measuring heat $[Q]$.

(a) *Heat measured in Thermal Units.*—The dimensions = $M\Delta$ (§ 75). Conductivity is called thermal conductivity, or absolute conductivity, and is represented by k , whose dimensions are—

$$M\Delta \div LT\Delta = \frac{M}{LT}$$

(b) *Heat measured in Thermometric Units*; that is, the heat required to raise unit volume of a substance 1° ; its dimensions are $L^3\Delta$. Conductivity is now called thermometric conductivity, or diffusivity, and is represented by $\frac{k}{c}$; for dimensions we have—

$$\left[\frac{k}{c}\right] = L^3\Delta \div LT\Delta = \frac{L^2}{T}$$

Remembering that c = specific heat \times density, its dimensions are therefore unity $\times \frac{M}{L^3}$. We obtain at once—

$$\left[\frac{k}{c}\right] = \frac{M}{LT} \div \frac{M}{L^3} = \frac{L^2}{T}$$

(c) *Heat measured as Energy.*—Dimensions $\frac{ML^2}{T^2}$

$$\therefore \text{dimensions of conductivity} = \frac{ML^2}{T^2} \div LT\Delta = \frac{ML}{\Delta T^3}$$

The results of research on conductivity have been given in varying units, and therefore it is necessary to translate them into one set of units for purposes of comparison.

Let us take Forbes's results (p. 217). His units of length and time are 1 foot and 1 minute.

The dimensions of $\left[\frac{k}{c}\right] = \frac{L^2}{T}$. 1 foot = 30.48 cm.; 1 minute = 60 seconds.

\therefore the multiplier, to change these numbers into diffusivity measured in the C.G.S. system, is $\frac{(30.48)^2}{60} = 15.48$

Ångström gives $72.96(1 - 0.00214t)$ for the diffusivity of copper. Units: 1 cm., 1 gram, 1 minute.

(1) To change into C.G.S. system, multiply by $\frac{1^2}{60} = \frac{1}{60}$

$$\therefore \text{diffusivity} = 1.216(1 - 0.00214t)$$

(2) To change into units used by Forbes (1 foot, 1 minute) (1 foot = 0.03281 cm.), multiply by $\frac{(0.03281)^2}{1} = 0.00108$.

$$\begin{aligned}\therefore \text{diffusivity} &= 72.96(1 - 0.00214t) \times 0.00108 \\ &= 0.078(1 - 0.00214t)\end{aligned}$$

To express this as thermal conductivity, we must multiply by c . The thermal capacity of 1 cubic foot of copper = mass of 1 cubic foot of copper \times specific heat.

Tait gives the thermal conductivity (k) of a specimen of copper as $4.03(1 + 0.0013t)$. Units: 1 foot, 1 minute, 1°C .

The thermal capacity of 1 cubic foot of copper = c = mass of 1 cubic foot of water \times specific gravity of copper \times specific heat of copper. Both the latter quantities will vary with the temperature, and should be determined for the bar used; taking ordinary values—

$$c = 62.51 \times 8.9 \times 0.0953 = 52.8$$

$$\begin{aligned}\therefore \text{diffusivity} &= \frac{4.03}{52.8}(1 + 0.0013t) \\ &= 0.076(1 + 0.0013t)\end{aligned}$$

To change this into C.G.S. units, we have—

$$\begin{aligned}\text{Diffusivity} &= 0.076(1 + 0.0013t) \times 15.48 \\ &= 1.176(1 + 0.0013t)\end{aligned}$$

[Compare Ångström, $1.216(1 - 0.00214t)$.]

147. Conductivity in Crystals.—Senarmont made a series of experiments to determine whether the conductivity of a solid was the same in all directions; this has been assumed to be true in the previous experiments. Thin sections were cut from crystals in various directions, a hole was drilled in the centre, and the sections were coated with wax. A stout copper wire was passed through the hole per-

pendicularly to the plane, and the wire was then heated by a lamp, screens being arranged so that the heat radiated from the lamp could not reach the section experimented upon. From the form of the area of wax melted deductions were made as to the conductivity in various directions. In the regular system of crystals the part melted was always circular, and it was inferred that the conductivity was the same in all directions. In the other systems the shape depended upon the system and upon the direction in which the section was taken compared with the principal axis. The shape was in



FIG. 91.



FIG. 92.

general an ellipse (Fig. 91), the major axis being in the direction of the principal axis.

The experiment can be conducted with greater care by heating the wire by a voltaic current.

148. Conductivity of Liquids.—The difficulty of preventing convection currents makes the experiments upon conductivity difficult and uncertain. Generally, the conductivity of liquids is low.

If the tube of a simple air-thermometer be passed through a bell-jar, as in Fig. 92, and the bell-jar be nearly filled with water, then, by floating a small dish containing alcohol on the top, arranging that the dish does not touch the sides, we can show that the conductivity of water is very small. On igniting

the alcohol, the steadiness of the index shows that no heat practically is being conducted through the water. If the bell-jar be filled with mercury, and the experiment be otherwise

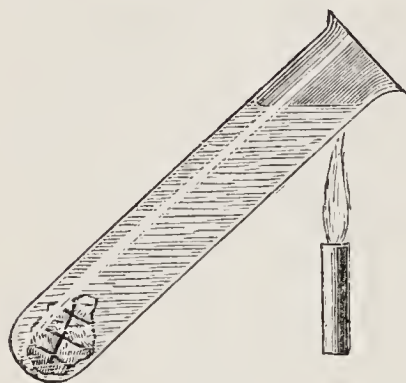


FIG. 93.

repeated, the index moves at once, showing that liquid mercury is, compared with water, a good conductor.

On account of the low conductivity of water, it is possible to heat to boiling the water at the top of a test-tube while ice (sunk by weighting with lead) at the bottom remains unmelted (Fig. 93).

Guthrie used two cones of platinum placed base to base; the lower one (Fig. 94) practically formed the bulb of an air-

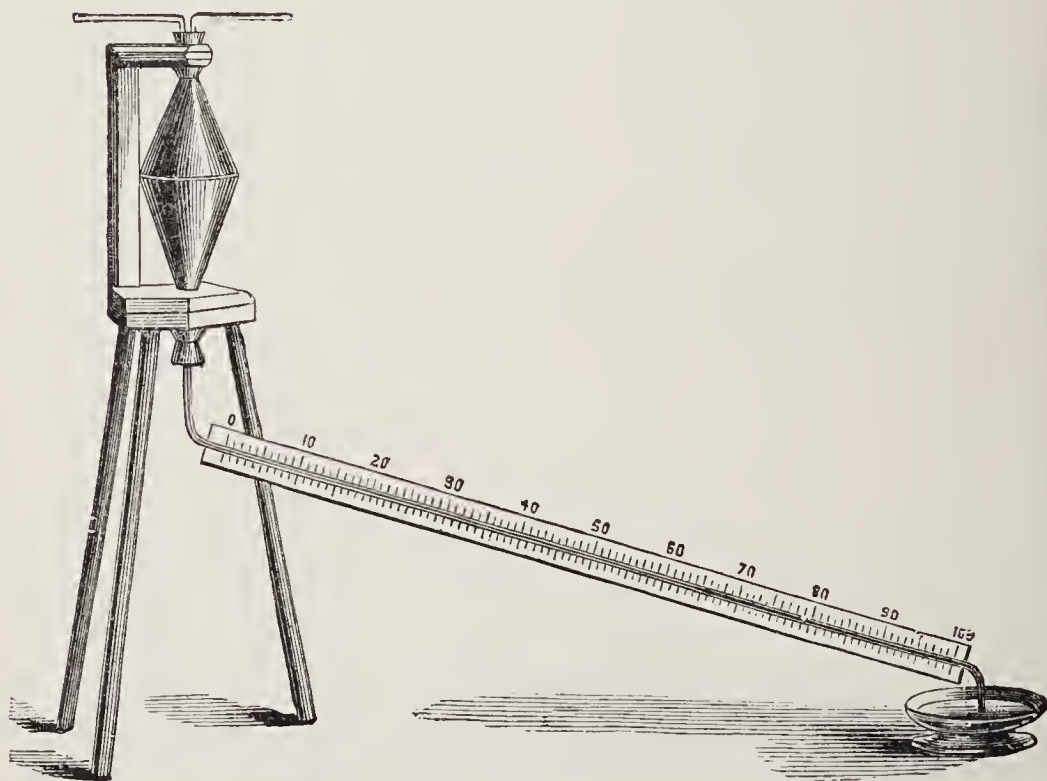


FIG. 94.

thermometer; water at a constant known temperature circulated through the upper cone. The liquid to be experimented upon was inserted in layers of known thickness between the cones, and the depression of the liquid in the graduated tube of the air-thermometer read.

The results show that, omitting mercury, water has the greatest conductivity among liquids, but that its conductivity is only $\frac{1}{95}$ that of copper.

CONDUCTIVITIES OF LIQUIDS (k).

Units : centimetre, gram, and second.

Water	...	0.00136	Ether	...	0.000303
Glycerine	...	0.000670	Alcohol	...	0.000423

149. Conductivity of Gases.—If a piece of lime be held in the hand, and one end be placed in the flame, the heat is conducted to the hand, and it is soon impossible to retain the lime. Let the lime, when cold, be powdered and placed on the palm of the hand ; a red-hot poker placed gently on the powder, although a very short distance from the palm, does not produce any uncomfortable sensation. The air between the particles of lime form a good non-conducting surface.

The conductivity of gases is much lower than that of liquids, and the difficulty of measuring is greatly increased by the convection currents. Certain results are obtained from experiments on cooling, and also from the kinetic theory of gases. The thermal conductivity of air is probably about

$\frac{1}{20000}$ that of copper.

CONDUCTIVITIES OF GASES (k).

Air	0.000048	Carbon dioxide	0.000040
Oxygen	...	0.000049	Hydrogen ...	0.000336
Nitrogen	...	0.000047		

The differences in the conductivities of metals, liquids, and gases make determinations on conductivity by the method of § 143 uncertain. Thus if we take the conductivity of air = 1, water = 30 (about), iron = 3500, and copper = 20,000. In measuring the temperature of the liquid, unless we get the exact temperature at the interface (this is generally almost impossible), we are measuring, in addition to the conductivity of the metal, that of a thin layer of water. This latter may

disguise altogether the result due to the metal alone. A similar remark applies to the passage of heat through an iron plate; a thin layer of air may offer a resistance to the passage of heat vastly greater than the resistance of the metal. For this reason the practical applications to boilers, etc., by utilizing numbers obtained from scientific research, must be made with caution, and should be checked with results obtained from actual observations. For practical purposes, the conductivity of thin plates of iron and copper is regarded as being perfect.

150. Applications.—Difference in conductivity is the cause of the different opinion we form as to the temperature of bodies (§ 1) when we test them with the hand.

It will be sufficient to give shortly a few further illustrations.

Water-pipes exposed to the weather are wrapped in straw, felt, etc., to prevent the loss of heat, and thus to avoid the consequences of the water in them freezing. Not only are the straw and felt bad conductors, but, being loosely packed, the air fills in the spaces, and it is, as we have seen, a very bad conductor.

If a piece of wire gauze (about 9 inches square) be held about 1 inch above the gas-tap, and the gas be then turned on, the gas can be ignited *above* the gauze; the gas below, however, does not inflame. The heat is conducted rapidly away by the iron wires forming the gauze, and is radiated so rapidly that its temperature never rises sufficiently high to ignite the gas that is in contact with it below.

The Davy and Stephenson's "Geordy" lamps are applications of this property. The burning wick is separated from the outer air by a closed cylinder of fine wire gauze. Air freely enters for the purposes of combustion, but the comparatively large area of gauze rapidly conducts the heat from any one part. The heat is radiated, and thus the temperature never rises high enough to inflame the combustible and explosive gases that may surround it in a mine. If the surrounding gas contains insufficient oxygen, the lamp goes out.

This applies to steady burning; the lamp is not perfect. Sound-waves, during blasting operations, may drive the flame through the meshes, or a draught may direct the flame on to

the gauze, and raise the temperature of a part sufficiently high to ignite the dangerous fire-damp.

Other examples will be given in the last chapter.

EXAMPLES. X.

1. Describe a few experiments which shall clearly illustrate and explain the principle and application of the safety-lamp.

2. What is meant by the conductivity of a body for heat? Show how the conductivity of a bar of iron may be accurately determined.

3. An iron boiler containing water at 100°C. is 3 cm. thick, and keeps a room in which it is placed at a temperature of 30°C. : if the conductivity of iron be 1.29 unit per hour, find how much heat is given off per hour from a square centimetre of surface.

4. How many gram-degrees of heat will be conducted in an hour through an iron bar 2 square cm. in section and 4 cm. long, its two extremities being kept at the respective temperatures of 100°C. and 178°C. , the mean conductivity of iron being 0.12? (The units are a gram, a centimetre, a second, and a degree Centigrade.)

5. How would you compare the thermal conductivities of brass and copper? Two equal cylinders, one of iron and the other of bismuth, are covered with wax and simultaneously placed on end on a hot plate. At first the melting of the wax advances more rapidly on the bismuth bar; but after it has melted about an inch up both cylinders, the melting advances the more rapidly on the iron bar. Account for these phenomena. (London Matric.)

6. Describe Forbes's experiments for determining the conductivity of iron. He finds the conductivity of copper at 200°C. is 0.00987. His units are the foot, pound, minute, the thermal unit, and degree Centigrade. Express the result in the C.G.S. units.

7. Explain the difference between "thermal conductivity" and "thermal diffusivity." What are the dimensions of each?

8. What objections have you to Example 3, based upon the conductivity of iron? What is the substance that is opposing the passage of heat?

9. Show the difference between thermal conductivity and diffusivity by means of the dimensions of these two quantities.

CHAPTER XI.

RADIATION.

151. Leslie's Differential Thermometer.—In experiments relating to radiant heat it is necessary to have a thermometer of great delicacy; the ordinary thermometers are unsuitable. The investigations of Leslie were conducted by the aid of the differential thermometer (§ 13), first constructed by him; one of the bulbs was blackened with lampblack, the better to absorb the heat. Many lecture experiments can be performed by its aid; particulars of some of these will be given. It is necessary to see that the thermometer is placed close to the radiating body.

152. Thermo-pile.—The differential thermometer has been displaced by the thermo-multiplier of Nobili. The apparatus as used consists of two parts—the pile and the galvanometer.

The galvanometer used is the ordinary astatic galvanometer (Fig. 100) or the Thomson mirror galvanometer.

The construction of the thermo-pile is based on the following experimental facts:—

Seebeck found that, if two bars of different metals be soldered together, and one of the junctions be heated, an electric current was produced.

In Fig. 95 *op* is a bar of bismuth, and *mn* a bent bar of copper. The apparatus is placed in the magnetic meridian. When one junction is heated, the needle *a* is deflected in such a manner that it indicates a current from bismuth to copper at the *hot* junction. If this junction be cooled by

melting ice, then a current is induced at the *cold* junction from copper to bismuth. The current increases as the difference between the temperatures of the junctions is increased.

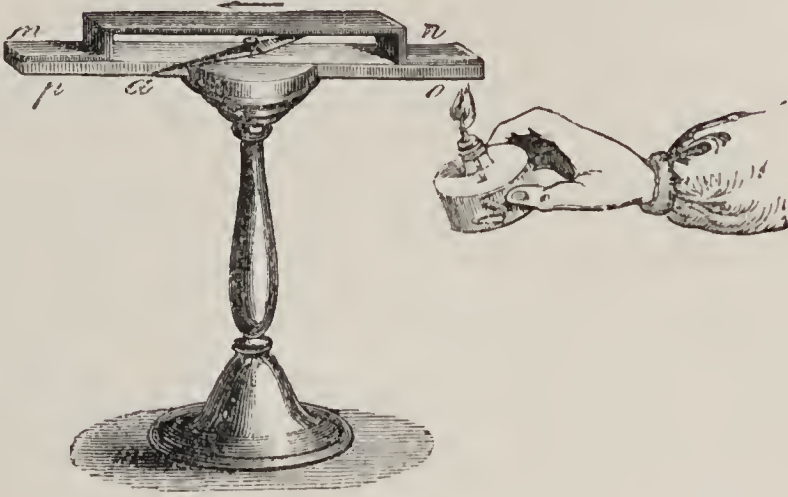


FIG. 95.

A similar effect is noticed if one junction only be soldered, while the other ends are connected by a copper wire (Fig. 96, where B is a bar of bismuth, A a bar of antimony, and C the soldered junction that is heated). The existence of the current is readily shown by connecting the unsoldered ends with the terminals of a galvanometer.

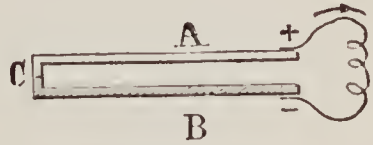


FIG. 96.

The best effects are produced by using antimony and bismuth as the two metals. The current is increased by taking a number of bars, and soldering them, as in Fig. 97, and heating

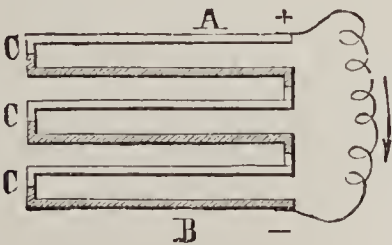


FIG. 97.



FIG. 98.

the alternate junctions. The letters have the same meaning as in Fig. 96.

In the thermo-pile small bars of bismuth and antimony are soldered together, as in Fig. 98, pieces of varnished paper

being placed between to prevent electrical contact. Several such sets are made (four in Fig. 99), and placed one above the other, each set being insulated from the other by the use of varnished paper or other insulator. In arranging the sets one above another, a bar of antimony comes above a bar of bismuth.



FIG. 99.

The bismuth *b* is then soldered to the antimony of the series above it; the bar of this second series with the free end will thus be bismuth. It is soldered to a bar of antimony of the third series, and so on. Thus, when complete, the only bars with a free end will be the antimony bar *a* and a bismuth bar of the top series. The pile, consisting of twenty pairs of elements, is enclosed in a copper frame, *P* (Figs. 99 and 100). Copper wires are fastened to the free antimony and bismuth bars, and, suitably insulated, are carried to the binding-screws *m*, *n*.

The binding-screws are connected with an astatic galvanometer, *G*, by wires, *a*, *b*. The junctions that are to be subjected

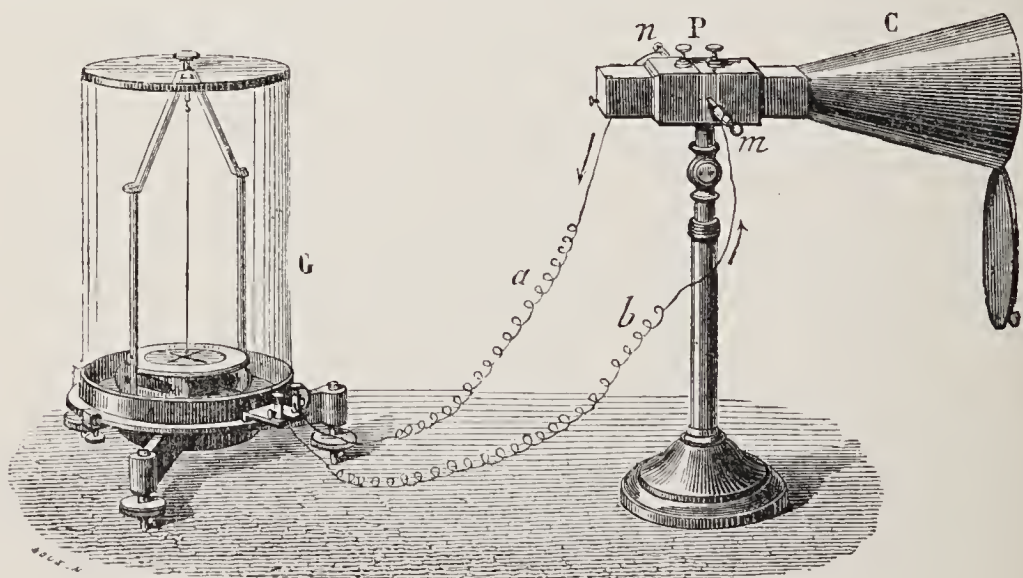


FIG. 100.

to any source of heat are usually surrounded by a cone, *C* (Fig. 100), in order to concentrate the heat-rays upon the face. In any experiment we shall have at the beginning both faces (*i.e.* both sets of junctions) at the temperature of the air, and

no movement will be observed in the galvanometer needle. If now the face enclosed by C be directed to any source of heat, the temperature of that face will be above or below the temperature of the air, according to the temperature of the source of heat; whether the temperature is above or below will be indicated by the direction in which the galvanometer needle moves.

For any temperature to which the pile will be subjected, the angle of deflection is proportionate to the heat that falls upon the pile.

It may simply be stated (for fuller details, the student should consult some work on electricity) that as heating a junction produces a current, heat-energy being given to the junction, if a current from a battery be sent across the junction in the direction of this original current (from bismuth to antimony), heat-energy is still absorbed and the junction is cooled. If by cooling a junction a current is produced, then, if a current from a battery be sent in this direction, the junction will be heated. This is called the **Peltier** effect.

153. Radiant Heat.—The transference of heat by convection and conduction leaves unexplained many phenomena. The heating of a room by a fire is not accompanied by currents from the fire to the sides of the room; and the interposition of a screen between ourselves and the fire, and the consequent shutting off of the heat, shows that the heat is not transmitted by conduction—the particles of air are not themselves perceptibly heated; there is no medium between the earth and the sun that can be utilized in transmitting the sun's heat by conduction or by convection; and furthermore, the speed with which the sun's heat reaches the earth—it travels with the velocity of light—shows that there is a different form of transference of heat from the comparatively slow method of conduction or convection. It has also been shown that heat is transmitted *in vacuo*; for conduction and convection some medium is necessary.

The identity of the two phenomena—light and heat—is further suggested by the fact that, after an eclipse of the sun, heat reaches the earth in the same time that light does.

It is believed that the heat of the sun, the heat from the fire or other hot body (save the small heat that may be transmitted by convection currents) is propagated as wave-motion. It is frequently called "radiant heat," but for the time being it is not heat at all, but simply wave-motion. The energy of the waves is converted into heat when they impinge upon any object. "Radiant energy," therefore, is a more accurate term than "radiant heat."

154. Wave-Motion.—Wave-motion is illustrated in the waves produced when a stone is thrown into a pond; alternately we have crests and hollows; the crests move forward, although the particles of water do not depart from their average position; particles of wood, etc., on the surface do not move forward, but have a movement that, on the whole, is up and down. The direction of the wave is at right angles to the motion of the water-particles. The waves that cross a field when the wind blows show strikingly how a wave can be transmitted, although the particles that compose the wave simply move around a certain fixed position.

By giving the necessary movement to the end of a rope, we can send waves of varying lengths along the rope.

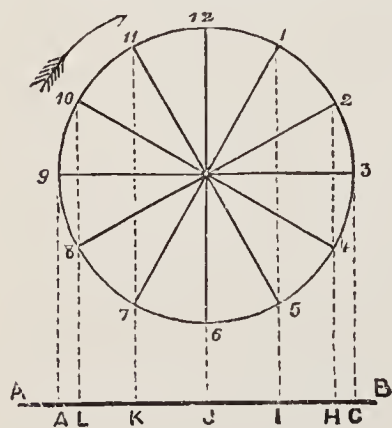


FIG. 101.

The idea of wave-motion will be aided by considering the motion of particles in a circle. Fasten a heavy bullet to a long fine string, and set the bullet swinging uniformly in a horizontal circle (Fig. 101, the plan of the circle 1, 2, 3, . . . 11, 12, is shown).

Place the eye in the same plane as the circle, so that the motion appears a straight line (A B). The motion from side to side is called an *oscillation*; from side to side and back again, a *vibration*, that is, the particle completes a revolution of the circle. By raising or lowering the eye, the path appears an ellipse, and the same terms can be applied.

The diameter (A L . . . H G) of the circle is called the *amplitude of the vibration*; and the time of a complete vibration, the *period of the vibration*.

The motion in the line, or in the ellipse, or in the circle, is called *harmonic motion*.

Let there be a number of particles moving in parallel straight lines, A, B, . . . R, S (Fig. 102), moving with harmonic motion, so that each succeeding particle begins to move a definite time behind the preceding one. Suppose, for example, that the period is one second, and that each particle begins

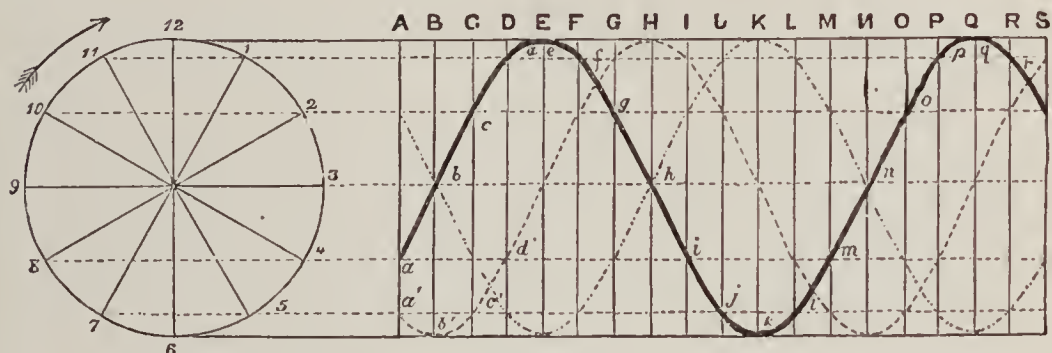


FIG. 102.

to move $\frac{1}{12}$ second behind the preceding particle. Draw the circle of given amplitude, and divide it into twelve parts. Let the particles in the line A be at *a*, *i.e.* at 4 in the circle, then the particle in line B will be $\frac{1}{12}$ behind, that is at *b*; the particle in C will be at *c*, etc. Join the points *a*, *b*, *c*, *d*, *e*, . . . and a sinuous curve is formed (the thick line). $\frac{1}{12}$ second, that is, $\frac{1}{4}$ period later, the particle in A will have moved from *a* to *a'* (*i.e.* in the circle it will have moved from 4 to 7); *b* will have moved to *b'*, etc. Join these points, and the dotted curve *a'*, *b'*, *c'*, *d'*, . . . will be formed; the crest has moved from E to H; the form of the wave is moving from A to S. The position $\frac{6}{12}$ second, or $\frac{1}{2}$ period from the beginning, is indicated by the curve — · · — · · — · ·. In $\frac{12}{12}$ second, or 1 period, the particles will be in their original positions, but the crest of the wave will have moved from E to Q.

The distance from crest to crest, or from hollow to hollow, is called a wave-length; or, more accurately, *wave-length* is the distance from any particle to the next particle that is in a similar position in its path and is moving in the same direction; thus from *b* to *n* is a wave-length. The wave-length can also be defined as the distance the wave travels in one period.

The student will see that similar results are arrived at if the particles, instead of moving in lines, moved in circles or ellipses.

Since the wave travels one wave-length in a period, to determine the velocity with which the wave travels, it is only necessary to determine the number of wave-lengths the wave has passed over in a unit of time.

$$\begin{array}{rcccl} \text{Wave-length} & \times & \text{number} & = & \text{velocity of propagation} \\ (\lambda) & \times & (n) & = & (v) \\ & & & & v = n\lambda \end{array}$$

Increasing the amplitude of the wave (making, in the illustration, the lines A, B, C, . . . longer) will not affect the speed of the wave as long as the period remains constant. The speed depends upon the period, not upon the amplitude.

The number of wave-lengths is evidently the number that will pass any point in one second (if 1 second be the unit of time); n , therefore, which measures the number of vibrations per second, also measures the frequency, or the number of times a wave will affect a stationary object in its path in a unit of time.

The speed with which radiant energy is transmitted varies with the density of the medium; it is less, for example, in air than *in vacuo*, less in glass than in air; but the number of vibrations keeps constant, therefore the wave-length varies with the speed. Wave-lengths, then, must always be referred to some standard subject (air) under given conditions or to *vacuo*. The quantity that does not change is the frequency (n).

155. Light and Heat.—It is believed that radiant energy is propagated by waves in which the particles of ether that fill all space move at right angles to the direction in which the waves move; this allows of great variety in movement—the particles may move in straight lines vertically or horizontally, or partake of both motions, or may move in circles or ellipses.

This is a brief but by no means complete statement of the method by which radiant energy is propagated; the whole process is probably much more complex than the illustration deduced from the oscillations of a single row of particles, and

the complete phenomenon is further complicated by the fact that waves of varying lengths are being propagated at the same time. For a fuller statement, as well as for the methods by which the wave-lengths may be estimated, some book on optics should be consulted.

The heat of a body is due to the kinetic energy of its molecules. Part of this energy is used in setting in motion the ether-particles that by wave-motion transmit the energy to other bodies ; in the process of transmission it is not heat, but simply a form of energy. The waves, on meeting a substance, may be retarded or destroyed. The energy of the wave may then produce certain effects : (1) it may increase the vibrations of the molecules of the new substance, that is, increase the kinetic energy, and therefore raise its temperature, or, if the substance be on the point of changing into the liquid or vapour state, the radiant energy may assist in the process, and thus increase the potential energy—in both cases acting as if heat were given to the new substance ; (2) falling upon a suitable substance, it may produce the effect of light, or, falling upon our eyes, it may produce the sensation of light ; or (3) the radiant energy may be able to decompose certain chemical compounds such as silver chloride. These effects are not sharply separated, and the total result of the radiant energy may be compounded of all three, that is, of heat, light, and chemical effects.

The wave-lengths are very small, and are usually expressed in millionths of a millimetre ($0.000001 = 1 \text{ mm.} \div 10^6 = 1 \text{ mm.} \times 10^{-6}$, written $1\mu\mu$). For the methods by which these measurements are made, some work on optics must be consulted. On account of its importance we may repeat that the velocity of radiant energy is lessened in passing through denser media, the wave-length becoming proportionately less. The number of vibrations or the frequency (n) remains constant. In defining a particular wave, either the frequency or the wave-length in a stated medium (air, for example) under given conditions as to temperature and pressure must be given.

The velocity *in vacuo* is, according to the best determina-

tion, 186,300 miles per second; this is nearly 300,000 kilometres per second = 3×10^{10} centimetres per second.

The wave-lengths that have been measured lie between $15,000\mu\mu$ and $290\mu\mu$.

All bodies that we are acquainted with are at some temperature; their molecules are therefore in a state of motion, and are able to start waves that transmit the radiant energy. The coldest bodies will therefore originate ether-waves that are comparatively long waves. The present methods of research can only detect waves, however, when their lengths are less than $15,000\mu\mu$. Until the last few years all waves shorter than $390\mu\mu$ and longer than $770\mu\mu$ were unknown. As the temperature of a body rises, shorter waves are added to the long waves already existing, and the combined effect, when these waves fall on a suitable object, is heat. When waves $2700\mu\mu$ in length are added, we are dealing with waves that we can detect in the radiant energy we receive from the sun. If we imagine that the temperature of a hot body continues to rise, waves whose lengths are $774\mu\mu$ begin (there is no sudden change in the lengths, the shortening is gradual), the total effect being, up to the present, that the radiant energy, when destroyed, is changed into heat. Waves shorter than $774\mu\mu$ produce a further phenomenon. Not only do they produce heat, but they affect the eye and produce the sensation of light, and the body which, up to the present, would in a dark room have been invisible, now glows with a dark red colour. As the temperature further rises, more heat is received, and it appears to the eye bright red, and ultimately it reaches a "white heat," or is incandescent: the last waves started are about $440\mu\mu$ long; they have not greatly increased the heat transmitted. A further rise in temperature starts yet shorter waves, but they add nothing to the heat transmitted as far as our instruments are able to measure, and they add nothing further to the light. Before incandescence was reached, the shorter waves were able to decompose silver chloride; the waves added after incandescence are peculiarly effective in this respect, and their effects can therefore be photographed by using silver chloride paper. We can by such means

determine the existence of waves whose lengths are $295\mu\mu$. Doubtless there are others whose lengths are yet less, but at present we have no means of detecting them.

Up to the present we have taken the combined effect of the waves. In § 167 it will be shown how these waves can be separated.

The important matter for the student to remember is that light, heat, and chemical action are effects due to one phenomenon—the transformation of the radiant energy of ether-waves; the effects vary with the lengths of the waves. It should be added that, in the above explanation, only the earlier known chemical effects are taken; with other substances than silver chloride, some of the shorter waves produce chemical effects. In heat we are concerned with the waves that produce the effect of heat; these, as is known at present, lie between $15,000\mu\mu$ and $290\mu\mu$. The greatest heating effects are produced by waves whose lengths are about $1100\mu\mu$ —waves unable to produce the sensation of light.

In the next few paragraphs we shall examine the total heat effects of radiant energy from any source; but most of the results will equally well apply to the heating effects of any particular waves.

156. Law of Inverse Squares.

—Radiant energy, in a homogeneous medium, travels in a straight line; and as a result of rectilinear motion we have the law that—

The heating effect varies inversely as the square of the distance.

If the source of heat at the centre, c (Fig. 103), of a sphere be very small, and supply an amount of heat whose measure is Q , then, the area of the sphere being $4\pi(ca)^2$, the quantity received

on unit area is $\frac{Q}{4\pi(ca)^2}$ If the heat falls on a sphere of

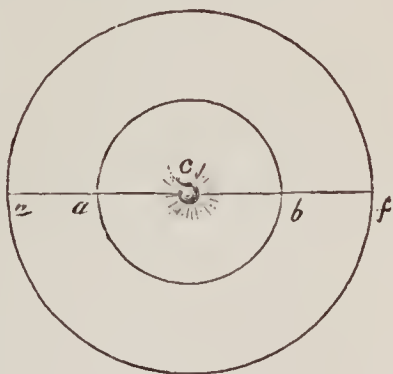


FIG. 103

radius ce , the quantity received on unit area is $\frac{Q}{4\pi(ce)^2}$

i.e. the amount received per unit area on the sphere ab :
amount received on the sphere ef =

$$\frac{Q}{4\pi(ca)^2} : \frac{Q}{4\pi(ce)^2} = \frac{1}{(ca)^2} : \frac{1}{(ce)^2}$$

This is experimentally verified by Melloni's apparatus.

A tin-plate box, M (Fig. 104), is filled with hot water, and is kept at a constant temperature; one side is coated with

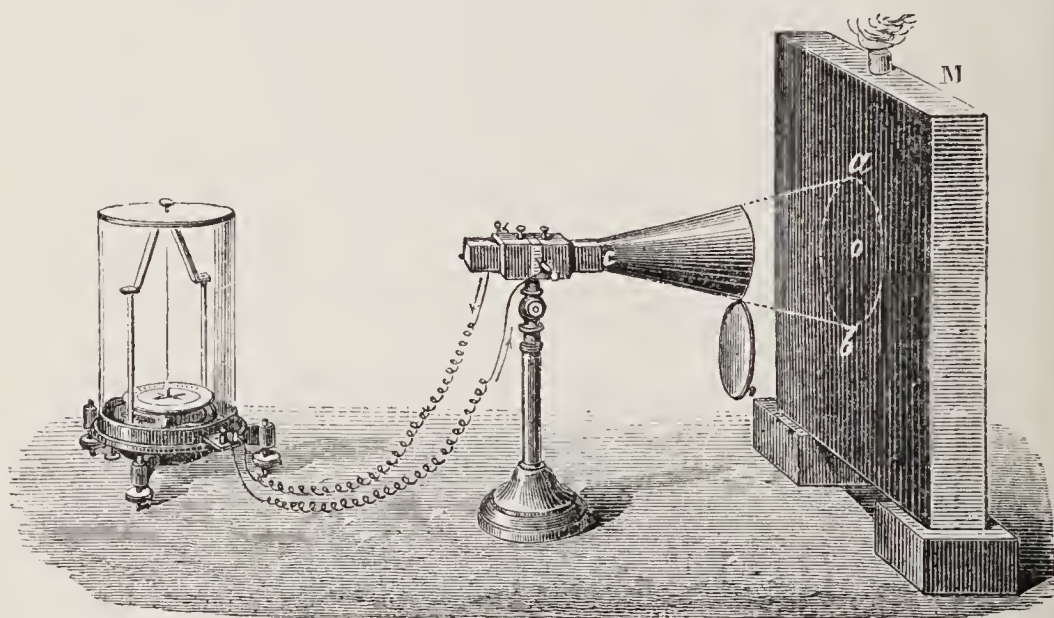


FIG. 104.

lampblack, and is directed towards the thermo-pile fitted with its conical reflector, and the deflection is noted at any given distance. The thermo-pile is now moved away, so that the base of the cone, ab , is enlarged to AB (Fig. 105). As long as the base of the cone falls on the lampblack surface, there is no change in the deflection, showing that the quantity of heat received per unit area in each case is the same.

The cones cab and CAB are similar. Since the temperature of the box is kept constant, the quantity of heat emitted will be as the areas of the circles ab and AB ; that is, as $(oa)^2$ is to $(OA)^2$, or (because the cones cab and CAB are similar) as $(co)^2$ is to $(CO)^2$. Since the quantities emitted are as the squares of the distances, and the heating effect on the thermo-pile is the same, the heat that falls on the thermo-pile must vary inversely as the square of the distance.

If the position of the galvanometer needle be noted when the box is in the position of Fig. 105, so that $C A B$ is a right

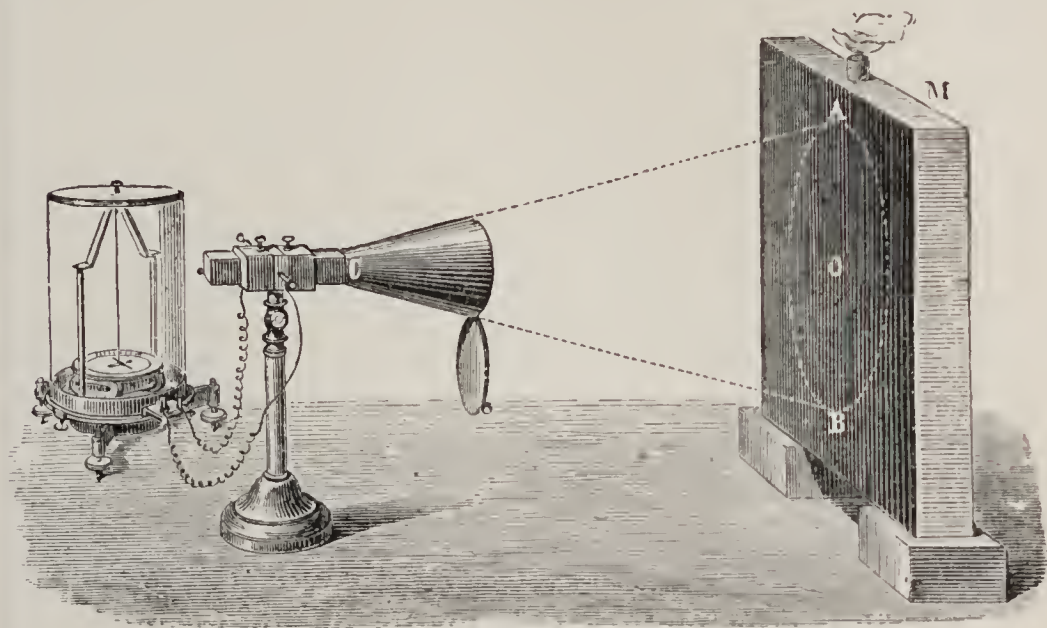


FIG. 105.

cone, and if the box be then slightly turned on a vertical axis through O , so that the base of the imaginary cone is still on the face of the box, then no change is made in the position of the needle.

157. Intensity.—The physical meaning of change of “intensity” for heat-rays, as long as their period remains constant, is that the amplitude of vibration has been changed. By doubling the amplitude, the intensity is quadrupled; by halving the amplitude, the intensity is reduced one-fourth; so that the intensity of heat varies as the square of the amplitude.

It has already been stated that radiant energy is transmitted by means of the vibration of the ether-particles. If we could see the motion of these particles, we should observe the greatest amplitude near the source of the radiant energy (a hot ball kept at a constant temperature, let us suppose); as we moved from the source of heat, the amplitude would decrease, the wavelength remaining constant. At double a given distance, the amplitude would be halved; at three times the distance, the amplitude would fall to one-third of the original amplitude.

158. Radiant Energy propagated in Vacuo.—The transmission of radiant energy is independent of air-particles,

and is due to the vibrations of ether-particles. That radiant energy can be transmitted through a vacuum is shown by an experiment due to Rumford.

A thermometer tube, t (Fig. 106), is sealed into a glass flask so that the bulb is at the centre. After softening and then narrowing the neck of the flask, a vacuum is produced by suitable means, and the tube is sealed. On immersing the flask in warm water, or bringing any hot body near, the thermometer at once rises. The effect could not be produced by heat being transmitted from the air by means of the glass of the flask or thermometer tube; it is transmitted by radiation through the vacuum in the interior.



FIG. 106.

The transmission from the incandescent carbons or platinum filaments of an incandescent lamp, and the effect of a hot body on the waves of Crookes's radiometer (§ 173), afford other illustrations of the fact that heat is transmitted *in vacuo*; and further, the fact that radiant energy from the sun reaches us can only be explained by assuming that air-particles are not necessary for the transmission of radiant energy.

159. Reflection.—If the waves by which radiant energy is transmitted meet a suitable surface, part are reflected. The laws that govern the reflection are—

(1) The incident ray, the reflected ray, and the normal of the surface are in the same plane.

(2) The angle of incidence is equal to the angle of reflection.

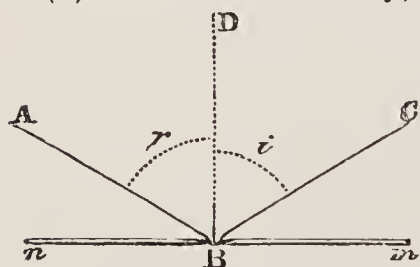
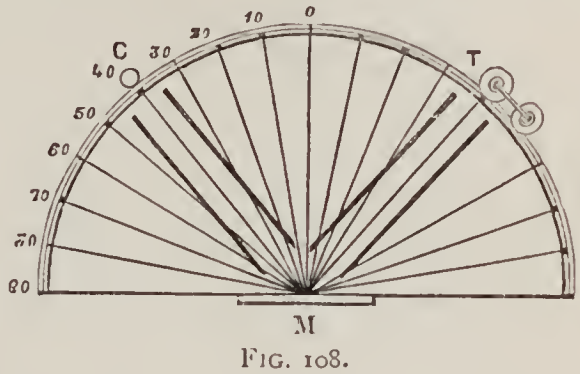


FIG. 107.

Let $m n$ (Fig. 107) be a plane reflecting surface, $B D$ the normal at the point B ; then if the ray of heat (or light) strike the surface in the direction $C B$, and be reflected as $B A$, $C B$ is called the incident ray, $B A$ the reflected ray; the angle $C B D$ is the angle of incidence (i), and $D B A$ the angle of reflection (r). $C B$, $B D$, $B A$ are in one plane, and the angle $C B D$ equals the angle $D B A$.

The laws as regards the waves that cause the sensation of light are readily illustrated by mirrors; for heat, simple modifications of such experiments are needed. The differential thermometer is sufficiently sensitive for rough experiments.

One bulb of the differential thermometer T (Fig. 108) is blackened to render it more sensitive. A semicircle, about $2\frac{1}{2}$ feet radius, is drawn on a table and graduated, and at the centre a sheet of tin, M, is placed vertically. Two tin tubes are directed towards M; at the end of one an iron ball at dull heat (C) is placed, at the end of the other the blackened bulb of the differential thermometer. The ball and its tube being fixed, the other, always directed towards M, is moved until the thermometer is affected.



Whatever angle one tin makes with the normal M o, the other makes an equal angle, and as all are in the plane of the table, the first two laws are demonstrated.

By keeping the source of heat constant (keep the ball in the flame of a large Bunsen burner), and substituting polished plates of brass, iron, similar roughened plates, and plates covered with lampblack, etc., at M, and noting the position of the index of the thermometer, we can roughly compare the reflecting powers of various materials. By such experiments substances have been arranged according to their comparative powers of reflecting heat.

Remembering that the finding of the position of the foci of concave mirrors is based on the laws of reflection, we can further verify the laws as regard radiant energy.

The foci of two concave mirrors are determined, and the mirrors are arranged facing each other (Fig. 109). At one focus, *n*, is placed a hot copper ball; a piece of phosphorus placed at the other focus, *m*, is at once ignited, or a small flask of water in the same position can be warmed. It can be shown,

by protecting m from the direct rays of n , that the heating effect is not produced by direct radiation.

If one of these mirrors be directed towards the sun, pieces of wood or paper are ignited at the focus.

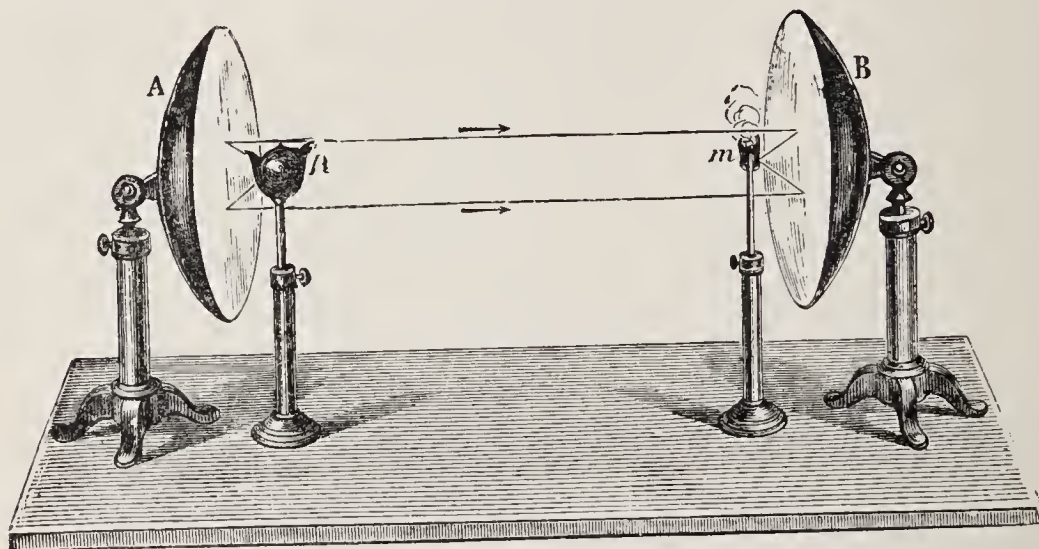


FIG. 109.

These experiments have been repeated by Davy *in vacuo*, thus illustrating the statement made in § 158.

If a flask containing melting ice or other cold body be placed at m , a thermometer placed at n falls in temperature. This apparent reflection of cold will be dealt with later.

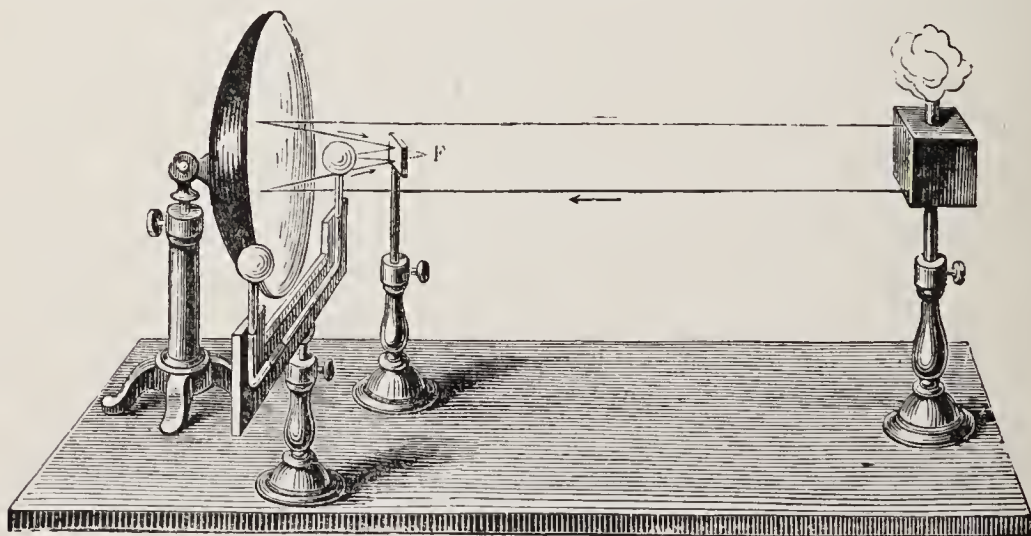


FIG. 110.

Suggestions have already been made for testing the reflecting powers of bodies. Leslie used a cube of boiling water, A, as a source of constant heat (Fig. 110). The rays, after reflection

at the concave mirror M, were received upon a small plane mirror of polished metal placed nearer to the mirror than the focus F; the heat-rays were thereby reflected and brought to a focus upon one bulb of the differential thermometer. By using different plane reflectors all of equal size, Leslie was able to assert that each mirror received equal quantities of heat, and that the varying effects upon the differential thermometer were due to the differences in the reflecting power of the substances used. By such means he obtained the comparative reflecting powers of various substances, making polished brass, which he regarded as the best reflector, equal to 100.

Polished brass	...	100	Indian ink	...	13
Silver	...	90	Glass	...	10
Steel	...	70	Oiled glass	...	5
Lead	...	60	Lampblack	...	0

Desains and De la Provostaye used Melloni's apparatus (Fig. 112). First the effect of a direct ray from a lamp was observed by noting the deflection produced in the galvanometer connected with the thermo-pile; then the effect was measured when the ray was reflected from various substances; in this way the ratio of the intensity of the direct ray to the intensity of a reflected ray was determined.

The reflecting power varied with the source of heat and varied also with the angle of incidence. When the source of heat was a Locatelli lamp, and the angle of reflection 50° , the following numbers were obtained :—

Silver plate	...	0.97	Steel	...	0.82
Gold	...	0.95	Zinc	...	0.81
Brass	...	0.93	Iron	...	0.77
Platinum	...	0.83	Cast iron	...	0.74

160. Diffusion of Radiant Energy.—If a ray of light in an otherwise dark room fell upon a piece of polished metal or a good mirror, the light is reflected regularly, and the surface can only be seen if the eye be placed in the line of the reflected ray. If the surface be rough—if, for example, the mirror be dusty, or a piece of paper take its place, then part of the light

is reflected irregularly, or is diffused, and the surface can be seen from any portion of the room. An analogous phenomena takes place with the obscure heat-rays. The thermo-pile is only affected in the case of perfect reflectors when it is in the path of the reflected ray. If the ray falls upon a surface like white lead or Indian ink, then the thermo-pile is affected in whatever position it is placed in front of such surfaces; the effect is obtained as soon as the ray falls upon the surface, and does not increase as the surface is heated, as it would do if the result were due to the heating of the surface and the consequent radiation.

The diffusive power of lampblack is practically *nil*, as is its reflecting power; the whole of the radiant energy that falls upon it is absorbed and radiated. The diffusive power varies with the source of heat; white lead, for example, has a marked diffusive power if the source of heat be at a high temperature, that is, if exposed to sun-heat or to the heat from incandescent platinum; when the source of heat is copper at 100° C., practically all is absorbed and none diffused. When sunlight falls upon ordinary objects, only certain light-rays are diffused; these produce the sensation of colour; the other rays are absorbed. Analogously, when sun-heat falls upon objects, certain of these rays are absorbed; the others are diffused, the rays diffused differing in various substances.

161. Emission, Absorption, Transmission.—The general facts regarding emission, absorption, and transmission are readily demonstrated.

If the cube (Fig. 110) be kept filled with hot water, and three of the vertical sides be coated with (1) lampblack, (2) paper, (3) isinglass, and (4) one side be kept polished, then, by bringing the hand in turn near each side, we can determine that the above order is the order of the powers of the substances as radiators. A bulb of a differential thermometer, blackened with lampblack (to render it a better absorber), shows the result more decisively; while the delicate thermo-pile answers yet better. Whatever be the measurer used, it should be held in turn at equal distances from each side.

A series of similar tin or brass vessels, coated on the

outside with different materials, may be filled once for all with equal quantities of hot water, and left to cool. By reading the thermometers placed in each vessel at equal times, we can determine which have lost the greatest amount of heat, and thus determine which substances radiate the more readily. Lampblack, and similar rough black substances, are the best radiators; to a less degree we have paper and roughened metals (by mechanical roughing or by oxidation), while polished metals are the worst radiators.

Place the vessels, with their bases covered with the substances to be examined, above a hot plate, kept at a constant temperature, or place them with their sides covered, at equal distances from the same source of heat (for rough purposes, at equal distances from a fire), fill the vessels with cold water, and examine the thermometers at the end of five minutes.

It will be found that the vessel coated with lampblack shows the greatest rise in temperature; next come those with surfaces like paper; and last, and worst, those whose surfaces are polished metals.

The substances, arranged according to their power of absorbing radiant energy, agree with their order as radiators.

It follows, therefore, that water boils the quicker in blackened kettles, while such a kettle, if removed from the fire, soon loses its heat. To keep water hot, it must be kept in polished vessels.

We have seen that lampblack, paper, rough metals, polished metals, are arranged in the reverse order of their reflecting powers, and we come to the generalization—

Good reflectors are bad radiators and bad absorbers.

Bad reflectors are good radiators and good absorbers.

The experiments of Leslie can also be performed by the student (Fig. 111). In comparing the radiating power, he kept his cube filled with hot water, and presented the faces covered with the substances in turn to a spherical mirror, M. His thermometer was placed in the focus F, and from the indications he constructed his table of the comparative powers of substances as radiators.

Melloni's apparatus being more delicate, the mirror was unnecessary. The rays passed through a hole in a screen (Fig. 112), and fell directly upon the thermo-pile.

In order to measure the absorbing power, he kept a constant source of heat, and allowed the rays to fall upon the

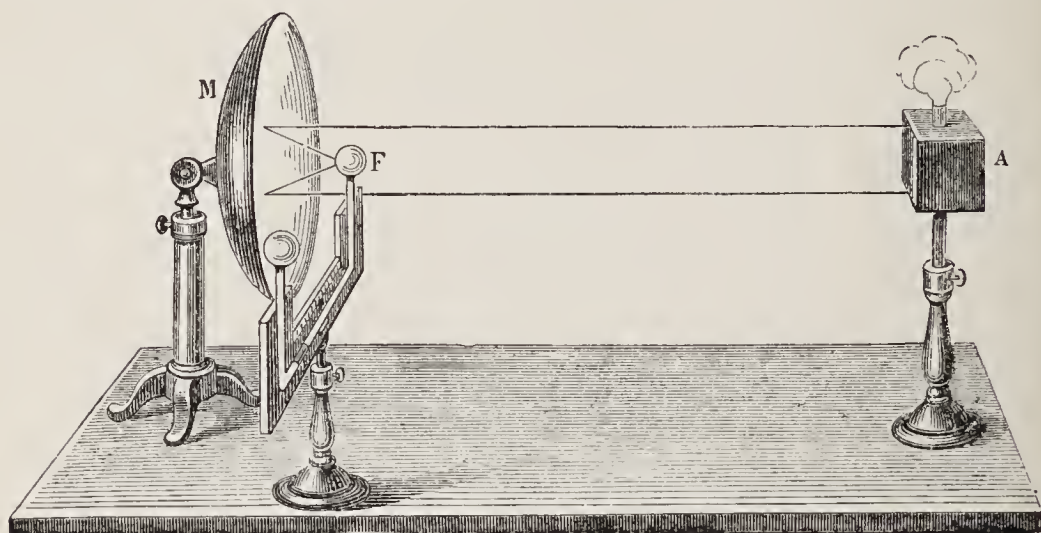


FIG. 111.

face of a copper disc covered with the given substance ; the other face was covered with lampblack, and beyond this was the thermo-pile. He found that the radiating power and absorbing power of a thick layer of lampblack was practically perfect. He called this power 100, and constructed the following tables :—

Emissive power. Temperature 100° C.			Absorbing power. Source of heat 100° C.		
Lampblack	...	100	Lampblack	...	100
White lead	...	100	White lead	...	100
Isinglass	...	91	Isinglass	...	91
Indian ink	...	85	Indian ink	...	85
Shellac	72	Shellac	72
Polished metal	3 to 17		Polished metal ...		13

162. Effect of the Source of Heat on Absorption.—

The experiments were repeated by varying the source of heat. Lampblack is taken as 100 at all temperatures.

The results are contained in the following table :—

Source of heat.

Substance.	Locatelli's lamp.	Incandescent platinum.	Heated copper.	Hot-water cube.
Lampblack ...	100	100	100	100
Indian ink ...	96	95	87	85
White lead ...	53	56	89	100
Isinglass ...	52	54	64	91
Shellac ...	48	47	70	72
Metallic surface	14	13.5	13	13

At high temperatures, Indian ink absorbs more than white lead, while at the temperature of boiling water white lead is equal to lampblack, while Indian ink has fallen from 96 to 85.

163. Diathermancy.—Just as substances like glass, crystal, sheets of paper, allow a certain amount of light to pass through, and are called transparent or translucent, while other substances, as metals (save when very thin), are opaque, so substances like glass, crystal, allow heat rays to be readily trans-

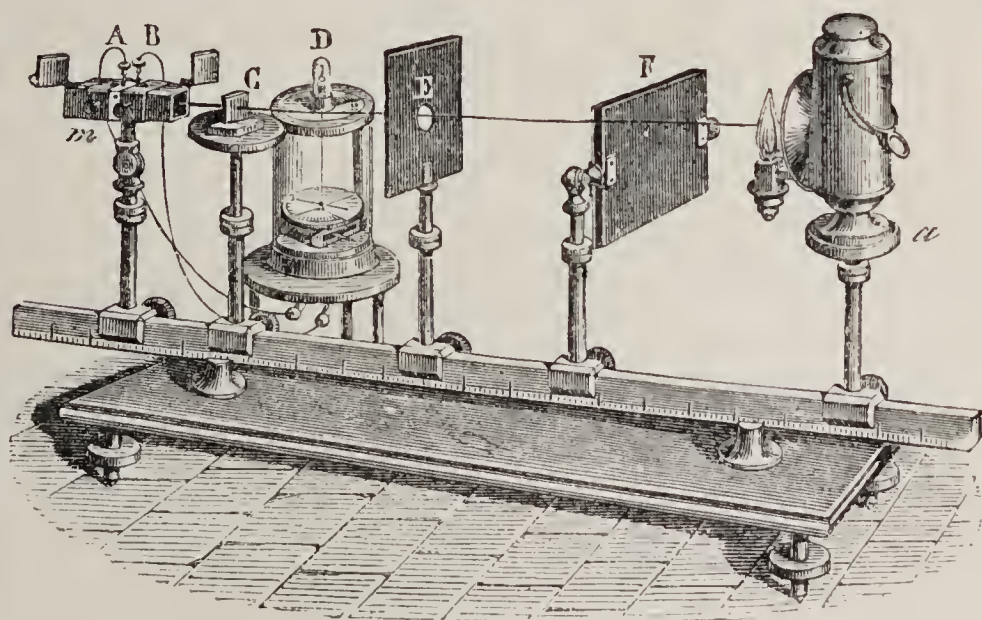


FIG. 112.

mitted, and are diathermanous; the term “adiathermanous” being used for bodies that do not transmit heat.

164. Transmission.—In the Melloni apparatus (Fig. 112) the rays from α , the source of heat, pass through the hole in the

screen E, and, after passing through a thin plate of the material, C, fall upon the thermo-pile A B *m*. The deflection of the galvanometer D is noted first before C is placed on the stand. This measures the total radiation (d) from the given source of heat. When C is interposed, the deflection (d') is again measured. Then the percentage of rays transmitted equals $\frac{100d'}{d}$

Liquids are enclosed in a trough whose sides are made of rock salt. The deflection is first measured when the trough is empty, then when it contains the liquid; the difference in the deflection measures the amount *absorbed* by the liquid, and by subtracting this from 100, the percentage of rays transmitted is obtained.

Gases were enclosed by Tyndall in a cylinder, A (Fig. 113), about 4 feet long, fixed horizontally, whose ends were closed

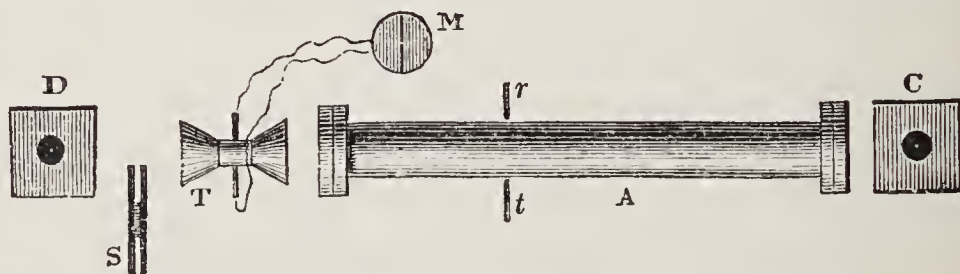


FIG 113.

by rock-salt plates. By means of the tube *r*, that was joined to a suitable pump, the cylinder could be exhausted, and the gas could then be admitted by the tube *t*. The thermo-pile T, and its galvanometer M, were at one end, and the source of heat C at the other. To increase the delicacy of his apparatus, in order to measure the very small percentage of absorption, another similar source of heat, D, was placed opposite the other end of the thermo-pile. By the aid of a screen, it could be so arranged that the effects of C and D were such that the galvanometer needle stood at zero when the cylinder was exhausted. The admission of a gas or vapour disturbed this equilibrium and the deflection, because heat was absorbed by the vapour; the radiation from the cube D had now the greater effect, and the deflection measured the absorption.

165. Melloni's Sources of Heat.—Melloni varied his experiments by using four sources of heat. These were (Fig. 114): (1) A Locatelli lamp with a compact wick, no chimney-glass, and provided with a reflector, L; (2) a spiral of

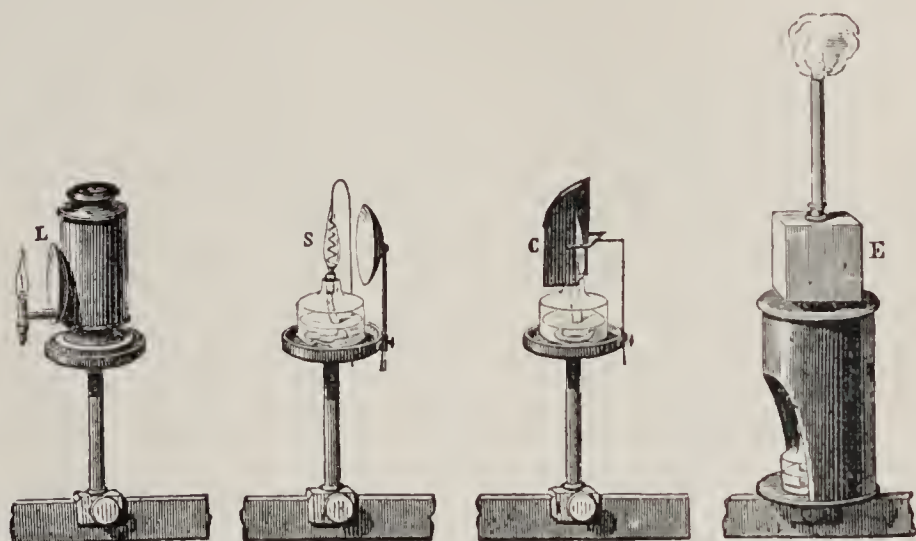


FIG. 114.

platinum, S, kept incandescent in the flame of a spirit-lamp; (3) a blackened copper plate, kept at a constant temperature (about 400° C.) by a spirit-lamp, C; and (4) a copper tube blackened with lampblack, E (kept at 100° C.).

166. Refraction.—When radiant energy meets a surface, part is reflected; another portion may enter the new medium, set in motion the ether-particles of the medium, and the wave continues its course. If the surface be perpendicular to the wave-front, the speed of the wave is diminished when it enters a denser medium; light, for example (the waves that affect the eye), travels with diminished speed through glass. If the wave-front makes an angle with the surface, as a consequence of the lessened speed, it swings round, so that the angle the direction of the wave makes with the normal is lessened. This phenomenon, known as refraction, is readily illustrated in the case of the waves that produce the effect of light. The beam of light, after reflection from the mirror M (Fig. 115), meets the surface of the water at C, making the angle BCN with the normal; part is reflected (CR), and part passes into the water as the beam CE ; the angle ECF is less than the angle BCN .

The ratio $\frac{\text{sine BCN}}{\text{sine ECF}}$ is the index of refraction, n , and is constant for the two media. In the case of air and water, $n = \frac{4}{3}$.

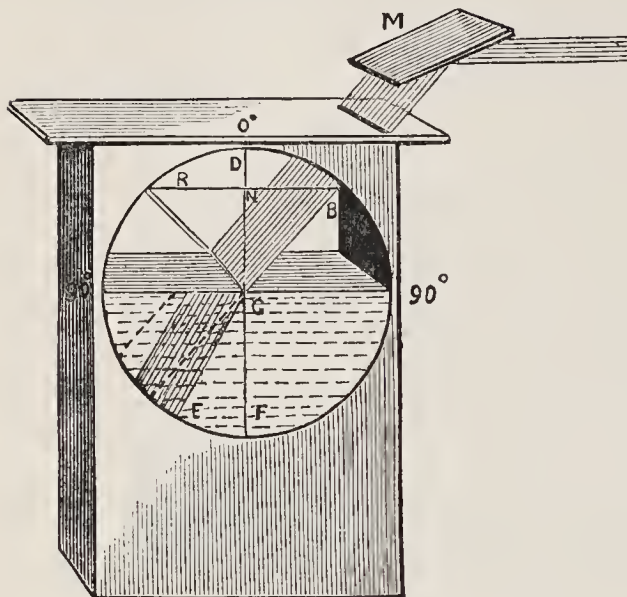


FIG. 115.

This expresses the fact that the speed of light in air is to its speed in water $:: 4 : 3$. This explanation applies strictly to waves of a definite length; but the dispersion is so slight in water that the ray of light may be considered as a whole. An analogous phenomenon is observable in the case of heat-waves.

The shorter the waves, the greater the refraction. Therefore the waves that produce the sensation of violet will be, after refraction, further from the normal than those that produce the sensation of red, and consequently a beam of white light is dispersed. (In the case of air and water the dispersion is so slight that it is difficult to observe.)

As a result of refraction, if the denser medium be in the form of a prism, after the beam has passed through it is found that its direction has been turned towards the base of the prism (see Fig. 116)—the shorter waves show the change of direction more than the longer ones.

167. The Spectrum.—This allows us to separate the waves. Light from a slit, *S* (Fig. 116), is focussed by the lens *A* on to the prism *B*. If the light, after emerging from the prism, be received upon a screen, the coloured spectrum is produced; the violet rays, *V*, are refracted the most, the red, *R*, the least. The spectrum from violet to red is visible to the eye; these colours are caused by the light-waves. The existence of rays refracted more than the violet (the actinic rays) is made evident by the effect on photographic paper, and the existence

of longer waves beyond the red, the so-called dark rays (from R to O), is proved by the use of the thermo-pile p .

A thermo-pile whose face was made of a number of elements in a line, was used in Tyndall's researches. Its face was

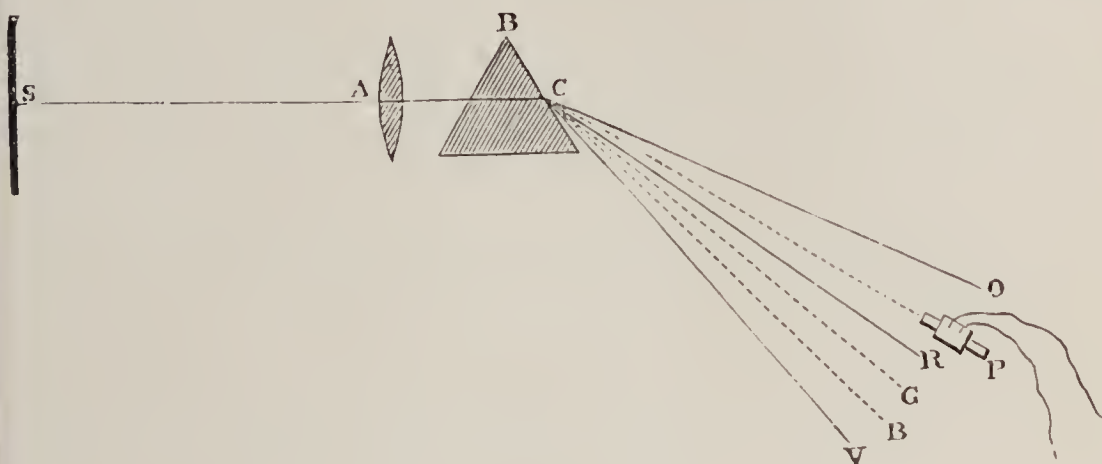


FIG. 116.

protected by a slit that could be made as narrow as was required. This face was moved along the spectrum, and the effect observed on a delicate galvanometer. The results were recorded as in Fig. 117. b (blue), g (green), y (yellow), o (orange), r (red), represent the visible spectrum from E to D.

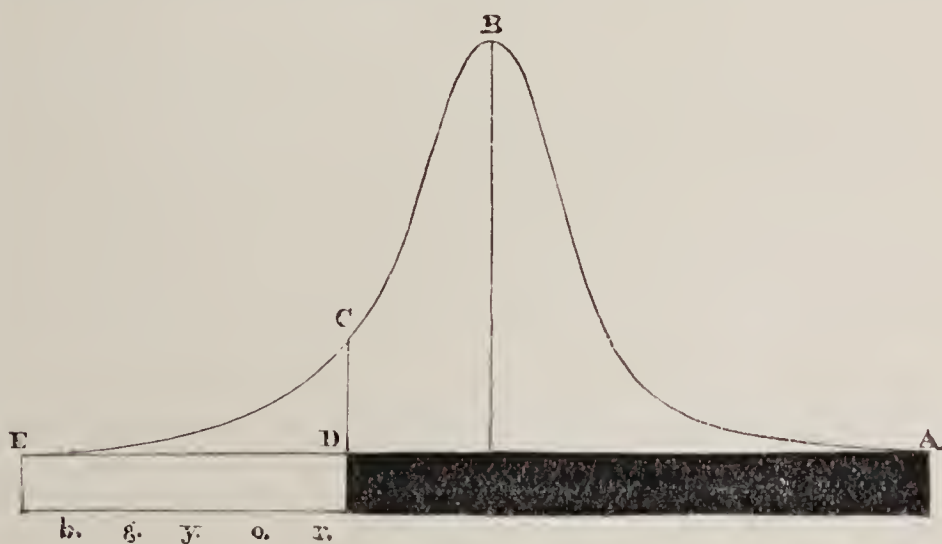


FIG. 117.

Vertical lines are raised proportional to the deflection indicated by the galvanometer, and a curve drawn joining the tops of these vertical lines.

The source of radiant energy was that of the electric arc,

the lens and prism were of rock salt, a substance that does not absorb the heat-rays. Beyond the blue (slightly) there is no heating effect ; there is a gradual increase towards the red ; but beyond the red, in a part that produces no effect of colour, we have a marked increase. A maximum is reached (B) at a distance beyond the red equal to one-half of the visible spectrum. There is then a decrease, the instrument ceasing to be affected at A, a distance beyond the red of twice the visible spectrum.

Fig. 118 is constructed in a similar way, but with the sun as the source of radiation. The light part is the visible

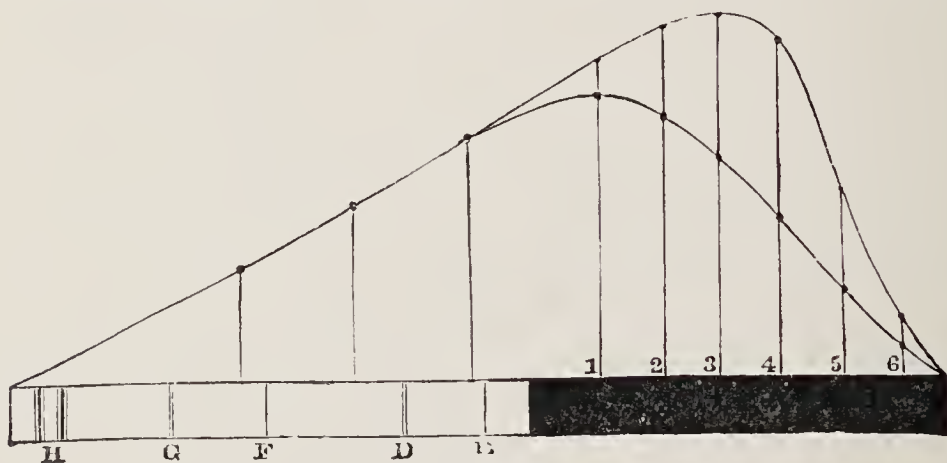


FIG. 118.

spectrum ; the dark, that beyond the red. With a rock-salt prism the upper curve was constructed, with a flint-glass prism the lower curve. We infer that flint glass stops part of the dark radiation. (What effect would you expect this to have on the temperature of the flint-glass prism ?)

Note, in the case of sunlight, that the dark spectrum, compared with the coloured spectrum, is much smaller than that obtained from the electric arc. This is due to the aqueous vapour contained in the atmosphere, and which absorbs the longer waves of the dark radiation.

The meaning of the letters H, G, F, etc. (Fig. 118), will be given later (§ 168).

The examination of the invisible spectrum beyond the red (called the ultra-red portion) has been greatly extended by Langley, who has invented a special instrument called a

bolometer (Fig. 119). By its aid differences of $\frac{1}{100000}$ of a degree Centigrade can be detected.

A current from a battery, B, passes to A, and there divides. The divided currents unite again at C. The wires carrying the divided currents are joined through a delicate galvanometer, G. a and b are two delicate coils made of iron ribbons $\frac{1}{50}$ of an inch wide and $\frac{1}{12000}$ of an inch in thickness. When the resistances of a and b are equal, and both are at the same temperature, no current passes through G.

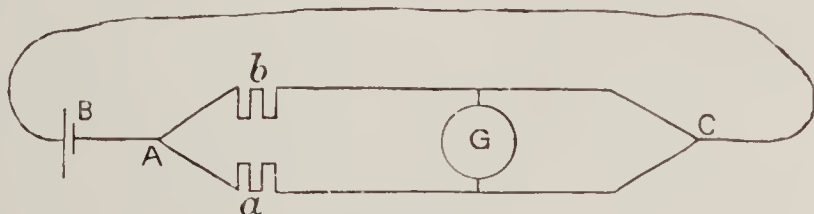


FIG. 119.

A delicate resistance-box (not shown) serves to make the resistances equal.

If one of the coils, say a , be heated, its resistance is increased, and a current passes through G. The apparatus in use is so arranged that the radiant energy passes through a narrow slit and falls upon a , the heating effect being measured by the deflection of the galvanometer. By moving the slit along the spectrum, the heating effect both of the visible and the ultra-red portions has been mapped out.

By substituting prisms of different materials, we can, by the construction of curves, come to some general conclusion as to the effect of such substances in absorbing the thermal rays. If, for instance, a water prism with sides of rock salt be substituted, then the maximum heating effect is in the visible spectrum. If the liquid be iodine dissolved in carbon disulphide, the visible spectrum disappears, but the heating effect can still be observed.

Bodies that transmit thermal rays are called *diathermanous*, rock salt being the best example; the term *adiathermanous* being used for substances that absorb thermal waves. Both

terms can also be applied to waves of a definite frequency. The portion of the thermal rays absorbed measures the absorption of the particular medium.

168. Selective Absorption.—If the strings of a piano be struck in turn, each produces a distinctive fundamental note. If now a note be sung or sounded near these strings, the string which, when struck, produced this note begins to vibrate, and the others remain unaffected. Singing the note sets the particles of air into longitudinal vibration, and waves of definite length are transmitted by the air. These waves strike all the strings, but only a particular string readily responds. If now this same note be sung into a large number of strings, each of which can respond, it is readily seen that the energy to start them must come from the sound-wave, which is thereby weakened, and we can even imagine a condition in which it will be altogether extinguished.

A similar selective power is observable in radiant energy. The spectra of incandescent solids and liquids are continuous; that is, there is no break in the visible spectrum produced, and, if the temperature can be raised high enough, the whole of the visible spectrum appears, save that the intensity of particular colours will predominate for separate substances. If in § 155 the body could be observed through a prism as its temperature rose, red would appear in the visible spectrum first, and would be gradually followed by the other colours, orange, yellow, green, blue, and finally by violet.

Instead of a continuous spectrum, brightly coloured bands, with dark spaces between, are obtained from vapours; the physical interpretation being that ether-waves of certain definite periods only are started by the glowing vapours. Sodium vapour, for example, if heated, starts waves whose lengths are, in air, about $589.5\mu\mu$ or $589.9\mu\mu$, their effect on the eye being to produce the sensation of yellow. Such rays, after passing through a prism, appear as two sharply defined yellow lines close to each other, in what would be the yellow portion of the complete visible spectrum. Now, suppose radiant energy from an incandescent solid to pass through sodium vapour; the radiant energy is being transmitted in waves of

varying lengths, but those nearly $589.5\mu\mu$ and $589.9\mu\mu$ long lose energy in starting the molecules of sodium vapour into motion; therefore the radiant energy, after passing through the sodium vapour, is deficient in these particular waves, with the result that, after passing through a prism, spaces or dark lines appear in the spectrum where the bright yellow lines would otherwise have been. On this account the solar spectrum is crossed by distinct black lines. The principal of these were first mapped out by Fraunhofer, and lettered A, B, C, D, . . . H (Fig. 118).

At such dark spaces, seeing that either no radiant energy or a smaller quantity than before is received, there will be a reduced heating effect. By his bolometer Langley has shown that dark spaces appear also in the ultra-red spectrum. From the existence of dark lines in the solar spectrum we infer that the radiant energy from the sun has passed through sodium and other vapours in its photosphere, and we can come therefore to conclusions concerning the composition of the sun and other astronomical bodies.

As illustrating this selective absorption, we may state that lampblack absorbs rays of all lengths: the absorption is total. Red glass absorbs all save the rays that produce the sensation of red; blue absorbs all save those that produce the sensation of blue; that is, each kind of glass selects certain rays. Rock salt is peculiarly diathermanous to the shorter waves, and thus, by using it in prisms, very little heat is lost. Alum readily allows the waves that produce light to pass, but absorbs nearly the whole of the ultra-red waves. If iodine be dissolved in carbon disulphide, a solution is obtained that is opaque to light, but which readily transmits the heat-waves.

The relation between the emissive and absorptive powers of bodies for radiant energy was stated by Kirchhoff, in 1860, in this form: The relation between the powers of emission and powers of absorption for rays of the same wave-length is constant for all bodies at the same temperature.

In the preceding sections the general results of radiation, as obtained from experiments, have been given. In the following sections considerations will be deduced from these

experimental results. It will be impossible to obtain in practice all the conditions that will be imagined; for perfect radiators, perfect absorbers, perfect reflectors of radiant heat, the existence of which will sometimes be assumed, are not at our command. The method that will be followed can be illustrated from mechanical studies. Questions relating to pulleys, for example, are discussed by imagining pulleys that work without friction, and cords that are perfectly flexible (neither condition can be attained); and the law deduced is applied to practical cases by introducing the effects of friction and rigidity. The subject might also have been treated by noting the relation between power and weight with the pulleys and ropes at our command, by making the pulleys as frictionless as possible, and by using cords as flexible as possible, by noting the relation between power and weight under these conditions, and finally determining the relation by imagining perfect conditions.

169. Newton's Law of Cooling.—The following conditions can be fulfilled: In a room without any fire or light, unexposed to the direct rays of the sun, the temperature of any part of the room will be the same, and will keep fairly constant. This is nearly attained in a room with a northern aspect at the basement of a building. Near the middle of such a room place a vessel containing water slightly above the temperature of the room, and insert vertically in the vessel a delicate thermometer. For this experiment a thin brass vessel that will contain about half a pint of water, fitted with a lid through which passes a delicate thermometer, is suitable. Note the temperature every few minutes, at first frequently, and try to determine the rate at which the water cools. Suppose the temperature of the room is 16° C., and the vessel is at 26° C., that is, there is a difference of 10° C. Note the number of seconds it takes the temperature of the vessel to fall one degree, that is, from 26° to 25° , from 25° to 24° , etc. In falling from 26° to 25° , the difference in temperature between the room and the vessel at the beginning is 10° , at the end 9° . Let us take $9\frac{1}{2}^{\circ}$, or 19 half-degrees, as the mean difference; some result like the following will be obtained:—

Fall in temperature of vessel.	Mean difference in temperature between room and vessel, in half-degrees.	Time, in seconds.
From 26° to 25° ...	19	60
„ 25° „ 24° ...	17	67
„ 24° „ 23° ...	15	76
„ 23° „ 22° ...	13	88
„ 22° „ 21° ...	11	104
„ 21° „ 20° ...	9	127
„ 20° „ 19° ...	7	163
„ 19° „ 18° ...	5	228
„ 18° „ 17° ...	3	380

Experiments can be made in any room shaded from the sun.

The general fact that the greater the difference in temperature the quicker the rate of cooling, is obvious; also that when the difference is 5 half-seconds, the rate is one-third of the value it has when the difference is 15 seconds. If we examine the relation between the rate of cooling and the differences in temperature, we obtain the following table:—

Difference in temperature, in half-degrees. t	Rate of cooling, in degrees per second. v	Ratio. $\frac{v}{t}$
19	$\frac{1}{60}$	$\frac{1}{60 \times 19} = \frac{1}{1140}$
17	$\frac{1}{67}$	$\frac{1}{67 \times 17} = \frac{1}{1139}$
15	$\frac{1}{76}$	etc. = $\frac{1}{1140}$
13	$\frac{1}{88}$	= $\frac{1}{1144}$
11	$\frac{1}{104}$	= $\frac{1}{1144}$
9	$\frac{1}{127}$	= $\frac{1}{1143}$
7	$\frac{1}{163}$	= $\frac{1}{1141}$
5	$\frac{1}{228}$	= $\frac{1}{1140}$
3	$\frac{1}{380}$	= $\frac{1}{1140}$

For the series of experiments we see that $\frac{v}{t}$ practically equals a constant (K) (average value nearly $\frac{1}{1141}$); that is—

$$v = Kt$$

This expresses Newton's law of cooling—that the rate of

cooling varies directly as the excess of the temperature of the body over that of the enclosure.

The rate of change of temperature of a vessel varies directly as the difference between the temperature of the vessel and the enclosure.

This "law" is fairly correct when the difference of temperature is small ; it does not apply when the difference of temperature is great.

$$v = Kt$$

The constant, K , will vary with the surface of the vessel, its area, the substance it contains, and the mass of the substance.

A series of experiments with the vessel slightly below the temperature of the room, say at 10° C., would show that the rate of heating of the vessel varied in a similar manner.

170. Dulong and Petit's Law of Cooling.—The essential parts of the apparatus of these two experimenters consisted of a small hollow brass sphere, into which fitted vertically a small metal cylinder. Through this could be passed and fixed an ordinary thermometer openly divided ; a closed glass tube slipped over the thermometer when in position. The inside of the sphere was blackened with lamp-black ; the interior was also connected with an air-pump. The sphere was placed in a vessel of water so that it was completely covered ; the water could be kept at any required temperature (for temperatures above 100° , oil could be used), being heated when necessary by passing steam into it. The brass was thin, therefore the temperature of the interior surface was that of the water, θ° .

The thermometer was taken out and heated until its temperature was about 350° C., then replaced so that its bulb was at the centre of the sphere, and the sphere was exhausted as far as practicable. Thus the conditions were a small body (the bulb of the thermometer) at a temperature, $\theta + t$ (t being the difference between the temperature of the enclosure and that of the thermometer), surrounded by an enclosure whose temperature was θ , the air between the two being exhausted.

Observations were made with the temperature of the water (and therefore that of the interior of the sphere) at 0° , 20° , 40° , etc. (called θ in the table below), and the relation between the rate of cooling and difference of temperature was calculated, the object being to ascertain whether Newton's law was independent of the absolute temperatures of the vessels.

Differences in degrees. t	Rate of cooling for various values of θ .			
	$\theta = 0.$	$\theta = 20.$	$\theta = 40.$	$\theta = 60.$
240	10.69	12.40	14.35	
200	7.40	8.58	10.01	11.64
100	2.30	2.74	3.16	3.68
10		1.40	1.62	1.88

Examining any horizontal line in the table, we see that the rate of cooling increases with the temperature of the enclosure, although a constant difference of temperature is maintained (see Table).

$$\frac{12.40}{10.69} = 1.16; \quad \frac{14.35}{12.40} = 1.16$$

$$\frac{8.58}{7.40} = 1.16; \quad \frac{10.01}{8.58} = 1.16; \quad \frac{11.64}{10.01} = 1.15$$

Proceed similarly with the other numbers to verify that the quotient is practically constant, and equal to $1.16 = c$.

Suppose we have found the absolute rate of cooling for any one of the differences. When the enclosure is at 0° , call this value μ ; then we can write any line as follows:—

Difference. t	$\theta = 0.$	$\theta = 20.$	$\theta = 40.$	$\theta = 60.$
Or	μ	μc	μc^2	μc^3
Or	$\mu c^{\frac{0}{20}}$	$\mu c^{\frac{20}{20}}$	$\mu c^{\frac{40}{20}}$	$\mu c^{\frac{60}{20}}$
Or, calling $c^{\frac{1}{20}} = a$	μa^0	μa^{20}	μa^{40}	μa^{60}

$$\therefore \text{rate of cooling } v = \mu a^\theta$$

where we have to determine μ , so that it will apply to any line.

Dulong and Petit made the assumption that the rate of cooling depended in some way upon the temperature of the thermometer ($t + \theta$) and upon the temperature of the enclosure (θ), and calculated that the velocity of cooling under any condition could be represented by—

$$v = ma^\theta(a^t - 1)$$

where θ is the temperature of the enclosure; t , the difference of temperature between enclosure and thermometer. m is a constant in any series of experiments, and depends upon the nature of the surface, the masses, and the kind of matter.

$$a^{20} = c = 1.16$$

$$\therefore a = \sqrt[20]{1.16} = 1.0077$$

temperature being measured on the Centigrade scale.

In arriving at this formula assumptions were made; its value, therefore, depends upon the question whether values calculated from the formulæ agree with the facts as obtained from experiments.

Suppose the temperature (θ) of an enclosure remains constant in a series of experiments, then—

$$v = ma^\theta(a - 1) = K(a - 1)$$

where K is a constant equal to $m(1.0077)^\theta$.

$$v = K(1.0077 - 1)$$

Giving t the values 1, 2, 3, etc., we obtain a table comparing v as determined by Dulong and Petit's formulæ, and as determined by Newton's ($v = Kt$), assuming that the two laws give the same result when the difference is 1° .

Difference of temperature.		Rate of cooling.	
		Dulong and Petit. $v = K(\alpha^t - 1)$	Newton. $v = Kt$
1°	...	0·0077	0·0077
2°	...	0·0155	0·0154
3°	...	0·0233	0·0231
5°	...	0·0391	0·0385
10°	...	0·0797	0·0770
20°	...	0·1658	0·1540

(All the numbers in the second and third columns should be multiplied by K.)

The difference is slight for small differences of temperature. Newton's result gives a value about $3\frac{1}{2}$ per cent. too low when the difference is 10° ; when it is 20° the value of the difference is 7 per cent. The error is so small for small differences that we may accept and use the simple law of Newton, but when the difference is more than 10° the divergence is too great to be neglected.

Other researches of Provostaye and Desains further verify Dulong and Petit's law within certain limits.

The student will remember that Newton's and Dulong and Petit's laws apply to the total radiation. The existence of air will produce air-currents, and heat will be transferred by convection.

171. Emissivity and Absorption.—"Thermal emissivity is the quantity of heat per unit of time, per unit of surface, per degree of excess of temperature, which the isolated body loses in virtue of the combined effect of radiation and convection by currents of air."

Therefore, the loss in time, t , will be—

$$Q = ES\theta t$$

S = area of surface, θ = difference in temperature between the body and the enclosure, t = time, and E a constant for the particular substance. E is the coefficient of emissivity, or

E will be the coefficient of absorption, if the body be below the temperature of the enclosure.

Macfarlane obtained the emissivity, in C.G.S. units, of copper, blackened and bright, in air, at ordinary pressure; the walls of the enclosure were blackened, and were at 14°C .

Differences of temperature.		Emissivity.			
		Polished surface.		Blackened surface.	
10°	...	0.000186	...	0.000266	
15°	...	0.000193	...	0.000279	
20°	...	0.000201	...	0.000289	
50°	...	0.000225	...	0.000326	

The meaning of one of the numbers, say 0.000356, is that when blackened copper at 64°C . is surrounded with damp air at atmospheric pressure enclosed in a vessel whose temperature is 14° , then the total loss of heat due to radiation and convection from 1 square cm. of the blackened surface is 0.000326 thermal unit ($\frac{1}{3070}$ nearly)

Professor Tait gives the following numbers obtained by Nicol:—

Hot body, 58°C .; enclosure, 8°C .; pressure of contained air in inches of mercury, (a) 30, (b) 4, (c) 0.4. *Units*: 1 lb., 1 foot, 1 minute, 1°C ., and the thermal unit.

		(a)		(b)		(c)
Bright copper	...	1.09	...	0.51	...	0.42
Blackened „	...	2.03	...	1.46	...	1.35

The numbers represent the total loss.

To compare these numbers with the above, we must change the units.

The dimensions of emissivity are obtained from $Q \div S\theta t$. The dimensions of $Q = M\Delta$, $S = L^2$, $\theta = \Delta$, $t = T$ (§ 75).

$$\therefore \text{the dimensions of emissivity } E = \frac{M\Delta}{L^2\Delta T} = \frac{M}{L^2T}$$

$$\therefore \text{for total loss for } \theta^{\circ} \text{ dimensions of total emissivity} = \frac{M\Delta}{L^2T}$$

$$\frac{(\text{lb.})(\text{C.}^\circ)}{(\text{foot})^2 (\text{minutes})} = \frac{(453.6 \text{ grams})(\text{C.}^\circ)}{(30.48 \text{ cm.})^2 (60 \text{ secs.})} = 0.00805 \frac{(\text{gram})(\text{C.}^\circ)}{(\text{cm.})(\text{secs.})}$$

\therefore the multiplier is 0.00805

Therefore from the last table we obtain at a pressure in millimetres of mercury: (a) 760, (b) 101.6, (c) 10.2.

	(a)		(b)		(c)
Bright copper ...	0.00887	...	0.00415	...	0.00342
Blackened ,, ...	0.01652	...	0.01188	...	0.01099

Dividing the first column by 50, we obtain the average emissivity per difference of 1 C.°: 0.000177 (bright), and 0.000330 (blackened), numbers that agree fairly with Macfarlane's.

172. Prevost's Theory of Exchanges.—The theory is that all bodies are radiating heat, whatever their temperature may be, and that the radiation depends upon the temperature of the body and the body itself, and not upon the temperature of surrounding objects. It follows that a red-hot ball radiates the same quantity of heat, whether in an ice-chamber or in the middle of a furnace, provided its temperature is the same in both experiences. Applied to a body in an enclosure, we have the result—the radiation of the body is independent of the temperature of enclosure. The enclosure is also radiating heat to the body; if the temperature of the body rise, it is receiving more radiant heat than it loses; if its temperature falls, it is radiating more than it receives; if the temperature remains constant, then there is a balance between the amount radiated and the amount absorbed. A warm body not only radiates heat to a mass of ice, but the ice radiates heat to the warm body (see § 159).

From highly polished metal surfaces the radiation, as we have seen, is very small. If we construct an enclosure with a bright metal exterior, then it radiates a very small amount; also, since it reflects all radiant heat, it absorbs little; if we further place a hot or cold body in such an enclosure at any temperature, then after a certain time the body and enclosure will be at the same temperature, and will both keep at that temperature. This is a fact that we deduce from experiments, when we eliminate as far as possible the gain or loss of heat

from external objects. The body is radiating heat to the enclosure, and is absorbing heat from the enclosure ; and as its temperature remains constant, its radiating power must equal its absorbing power, whatever the nature of the body may be (compare the construction of a good calorimeter). This is dealing with the total radiation. It is also true of any particular part of the radiation. Stewart illustrated this by examples similar to the following :—A piece of blue glass ordinarily appears blue because it absorbs the longer light-waves (*i.e.* the red) and transmits the blue. If such a piece of glass be placed in the middle of a fire, its blue colour seems to disappear, and it cannot be distinguished from the surrounding hot portion of the fire. It still transmits the blue rays, but, being heated to a high temperature, it radiates also red waves ; these two together produce the sensation of reddish white. To further test this theory, if the hot glass be taken into a dark room, it no longer appears blue, but reddish, *i.e.* it is radiating the waves it previously absorbed.

173. Crookes's Radiometer.—A glass tube is blown into a globular shape at its upper part (Fig. 120). Into the lower part is fused a thin upright glass tube, that, fitted into a wooden stand, supports the whole of the apparatus. A fine steel point is fused into the upper part of this tube, and on the point rests a small glass or agate cap. To the cap are attached four aluminium wire arms in a horizontal plane, making a right angle with each other ; the arms carry small diamond-shaped discs of mica, each in a vertical plane. A glass tube is fused into the upper portion of the apparatus, its purpose being to keep the cap in position when the whole is moved about ; the cap, however, does not touch this tube when the discs are moving. The upper end of this tube is open, and, by connecting it with a Sprengel pump, the air inside the instrument can be exhausted ; the opening is then sealed. The aluminium discs are covered on one side with lampblack, the other side remaining bright, and they are so arranged that a black side is always followed by a bright side as we move round the four discs.

If the instrument, as ordinarily sold, be exposed to a

source of radiant energy, the discs move in such a way that the black sides move away from the source of the radiant energy, which may be a lamp, the sun, etc. ; the greater the radiant energy, the quicker the rate of revolution. Thus, by considering the number of revolutions and the distance of the source, the intensity of the radiation may be measured.

If the opening at the top be kept open, and connected with a pump, so that the amount of exhaustion can be regulated at will, then for any source of radiant heat it is found that, after a certain degree of exhaustion, the following results are observable: The black discs are repelled, and rotation ensues. If the exhaustion be gradually increased, a maximum speed is reached ; further exhaustion diminishes the number of revolutions, and ultimately the rotation ceases.

Crookes showed that the best effects were obtained if the globe were as small as possible. It has also been shown that, if a specially constructed instrument of great delicacy be made with brass discs, and floated in water, and if the discs be kept in position by a strong magnet, then, when radiant energy acts upon the discs, the globe rotates in the water. This shows that the action and reaction must take place between the disc and the glass globe, and not, as it might appear, between the discs and the source of light or heat.

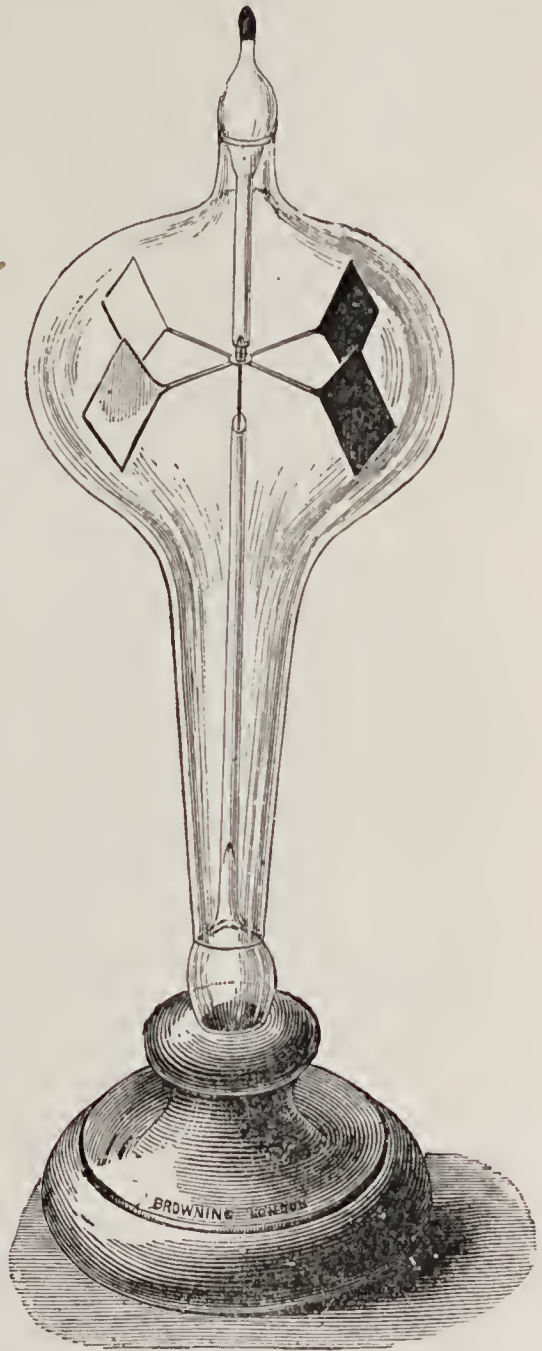


FIG. 120.

The experimental results show that, in the working instruments, there is not, as was at first supposed, a perfect vacuum, but that there is in all cases a residue of gas or air left.

The molecules of gas or air are moving about in all directions, with a speed that depends upon the temperature (§ 77). If the degree of exhaustion be sufficient, the molecules possess a free mean path equal to or greater than the distance between the disc and the surface of the glass ; that is, a molecule, after impinging upon the discs, does not collide, as a rule, with any other molecule before reaching the glass.

When subjected to any source of radiant energy, the black side absorbs more heat than the metal side ; the temperature of the black side is therefore greater than that of the metal side.

Let us suppose that at the beginning a black side of one disc and the metal side of a disc two right angles away are directed towards the source of heat or light, we can then neglect the heating effect on the other two discs. The molecules at first are impinging on all sides of all the vanes with equal speeds, and are rebounding with the same speeds. When the source of light or heat is brought near, the temperature of the black side rises above that of the metal side ; therefore the molecules will be heated and will rebound with greater speed from the black side ; this recoil is thus greater than the recoil from the metal side, and, by the third law of motion, the disc, being free to move, will move so that the black side moves away from the source of light or heat. The action continues to a less degree when its surface makes an angle with the direction in which the radiant energy moves ; another disc is brought into position, and a continuous rotation ensues. If the radiometer be now further exhausted, there are fewer molecules ; the difference between the effects of the bombardment on the two sides will be lessened, and the speed of rotation will be diminished. Ultimately the difference will be insufficient to overcome the slight friction, and rotation ceases.

174. Solar Radiation.—To determine the solar radiation, Pouillet constructed an instrument called a pyrheliometer.

It consists of a cylindrical vessel of thin metal, highly polished (Fig. 121). The upper surface is covered with lampblack. The bulb of a thermometer is inserted in the cylinder, which is otherwise filled with water; the stem of the thermometer is further enclosed in another tube. The lower disc is of the same diameter as the cylinder; its use is to ensure that the blackened face is turned directly towards the sun. When this is the case, the shadows of the cylinder and the disc will coincide.

The instrument at the beginning of an observation is shaded, and is at the temperature of the air. The lamp-black face, carefully shaded from the sun, is now turned towards the sky for a definite time (t units); radiation takes place, and the temperature falls θ degrees.

The face is now turned towards the sun for the same time; the temperature rises Θ degrees. It is next turned towards the sky, as at the first, for the same time, and the temperature falls θ' degrees.

During the time it was turned towards the sun it absorbed and also radiated heat. The fall in the temperature due to the radiation for the time when its initial temperature is that of the air is θ degrees; when the initial temperature is the highest point registered, it is θ' . It is assumed that the total radiation during the exposure to the sun is the mean of these two; that is—

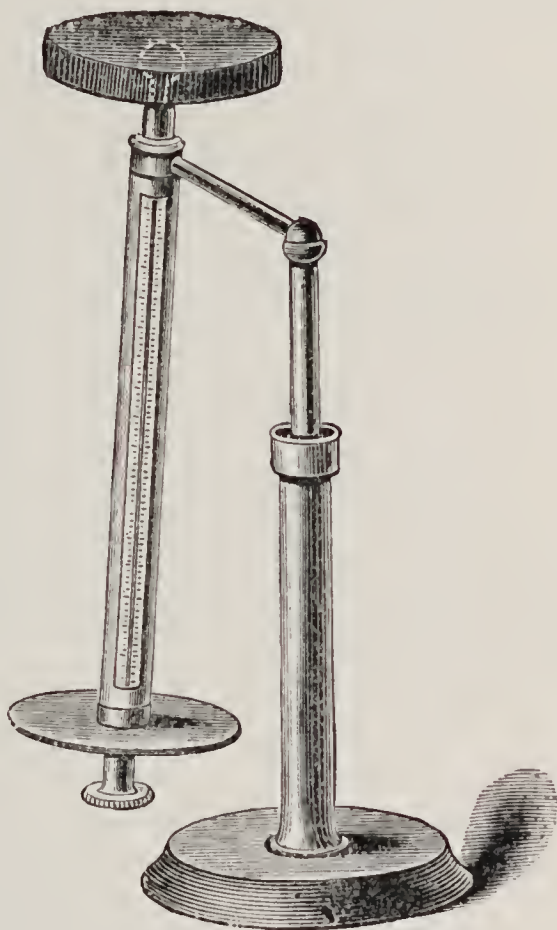


FIG. 121.

$$\frac{\theta + \theta'}{2}$$

Therefore the total rise of temperature that would have been registered if there had been no radiation would have been—

$$\Theta + \frac{\theta + \theta'}{2}$$

When radiant energy from the sun falls upon an area equal to that of the lampblack face (A), it is able to raise the temperature of the vessel $\Theta + \frac{\theta + \theta'}{2}$ degrees. The water equivalent of the vessel, the water, and the thermometer bulb can be calculated. Let it be ω . Then the radiant energy received per unit area per unit time is—

$$\omega \left(\Theta + \frac{\theta + \theta'}{2} \right) \div At$$

Radiant energy is absorbed by the atmosphere, and Pouillet attempted to determine the effect of the thickness of the atmosphere upon the heat we receive from the sun, and concluded that not more than one-half of the total radiation reached the earth.

We are able to measure the unabsorbed radiation that reaches us in units of heat per unit area per unit of time, and, by using Joule's equivalent, are able to calculate the energy in mechanical units.

If the whole were employed in melting ice, it would in a year melt a layer of ice all round the earth 35 yards in thickness. Other calculations state the unabsorbed energy as equal to 133 foot-pounds per square foot per second.

Only a fraction of the sun's heat reaches the earth. Sir William Thomson's estimate is that the total energy of the sun is emitted at the rate of 7000 horse-power per square foot.

EXAMPLES. XI.

1. Explain the terms "wave," "wave-length," "frequency," "amplitude."

2. The sun radiates his heat towards the earth, and the earth radiates her heat through stellar space: do you suppose that the solar and terrestrial heat passes with the same ease through the earth's atmosphere? Give the effect of your answer on the temperature of the earth.

3. Give an example of a good and a bad radiator ; also of a good and a bad absorber ; and state the general relation that exists between radiation and absorption.

4. If two planets of equal size be placed, one at 100, and the other at 200 millions of miles from the sun, compare the heat received by each per unit of surface. Imagine and describe an atmosphere by which, if the distant planet be surrounded, its temperature will become equal to or even greater than the near one.

5. A very sensitive thermometer has its bulb covered with lampblack in ordinary air ; a current of perfectly dry air, of precisely the same temperature as the surrounding atmosphere, is urged very gently against the bulb ; the thermometric column sinks : why ? On stopping the current of dry air, the column instantly rises : why ?

6. Explain how to determine the emissive powers and the absorbing powers of substances for radiant heat, and state the relations which exist between them.

7. Explain the terms "radiant light" and "radiant heat." What objections can you raise to the terms ?

8. Explain why the temperature of a greenhouse is above that of the surrounding air. (The greenhouse is unheated.)

9. How could you separate the dark radiation of an arc light from the luminous radiation ? and how could you demonstrate the existence of the longer rays ?

10. Compare Newton's with Dulong and Petit's law of cooling. How would you experimentally demonstrate the laws ?

11. Describe and explain the action of Crookes's radiometer.

12. Illustrate the term "selective absorption."

13. A thermometer placed in an open black box, and exposed to the sun, rises to 80° F. ; a glass cover is placed on the box, and the temperature rises to 120° F. : explain this, and apply your explanation to the possible influence of a planet's atmosphere in augmenting its temperature.

14. Explain Prevost's theory of exchanges, and apply it to the apparent "radiation of cold," in § 159.

15. The total emissivity of glass at 100° C. per square foot per minute to an enclosure at 0° C., is 0.176 thermal unit (unit of mass is 1 lb.). Change this into C.G.S. units.

CHAPTER XII.

THERMO-DYNAMICS.

175. First Law of Thermo-dynamics.—The mechanical equivalent of heat has already been determined from Joule's experiments to be 772 foot-pounds when degrees are measured on the Fahrenheit scale, and 1390 foot-pounds when the Centigrade scale is used (§ 76), and from such experiments the first law of thermo-dynamics is deduced—

“When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence, or are generated.”

$$W = JH$$

176. Mayer's Experiments.—Mayer determined the mechanical equivalent of heat from observations on gases. His method is illustrated in the next paragraph.

The following experiment is supposed to be performed when the atmospheric pressure is normal, that is, 14.7 lbs. on the square inch. Imagine a long hollow cylinder placed vertically, closed at the bottom; the internal section is 1 square foot. A weightless piston fits exactly into the cylinder and slides in it without friction. This piston cuts off 1 cubic foot of dry air at 0° C. and 14.7 lbs. pressure; that is, the piston is 1 foot from the bottom of the cylinder.

The area of the piston is 144 square inches; therefore the total pressure on the piston is $14.7 \times 144 = 2116.8$ lbs.

Suppose heat to be supplied to the imprisoned cubic foot of air sufficient to double its volume.

The coefficient of expansion being $\frac{1}{273}$, we know that the temperature will be 273° C. when the volume is doubled.

The external work is that done in overcoming a pressure of 2116.8 lbs. through 1 foot, that is, 2116.8 foot-pounds of work.

The thermal units needed to raise the temperature of the confined air from 0° to 273° C. and to do the external work will equal the product of mass, specific heat at constant pressure, and 273.

The mass of 1 cubic foot of air at 0° C. and at atmospheric pressure is 0.081 lb. The specific heat of air at constant pressure is 0.237.

\therefore the thermal units used in (1) raising the temperature, that is, in increasing the kinetic energy of the particles, and (2) doing external work $= 0.081 \times 0.237 \times 273 = 5.241$ thermal units

\therefore 5.241 thermal units have done work—

(a) Internally, by raising the temperature ; and

(b) Externally, against the atmosphere.

Now, imagine the cubic foot of air again at 0° C. and at normal atmospheric pressure, but enclosed in a rigid vessel, so that expansion, and therefore external work, is impossible. Under such conditions the specific heat of air (at constant volume) is 0.168.

\therefore the thermal units required to raise the temperature from 0° to 273° C. at constant volume $= 0.081 \times 0.168 \times 273 = 3.715$ thermal units

Th. units	Internal work.	External work.
$5.241 =$	$\left\{ \begin{array}{l} \text{raising the temperature} \\ \text{from } 0^{\circ} \text{ to } 273^{\circ} \text{ C.} \end{array} \right\}$	$+ 2116.8 \text{ foot-pounds}$
$3.715 =$	$\left\{ \begin{array}{l} \text{raising the temperature} \\ \text{from } 0^{\circ} \text{ to } 273^{\circ} \text{ C.} \end{array} \right\}$	$+ 0 \quad ,$
$\therefore 1.526 =$	0	$+ 2116.8 \quad ,$

$$\therefore 1 \text{ thermal unit} = \frac{2116.8}{1.526} \text{ foot-pounds}$$

$$= 1387 \quad ,$$

Mayer's first published results were inaccurate, but this arose from the errors in the data he took from the experimentalists. With the use of later values of the specific heats of air, results are obtained that fairly approximate towards Joule's number.

There is an assumption in the reasoning that prevents the conclusion being a logical one. It is assumed that the energy necessary to raise the temperature from 0° to 273° C. without increase in volume, is equal to the energy required to raise the temperature from 0° to 273° C. when the volume is doubled, provided that in expansion the air does not overcome external resistance. We can write, for example, the first line thus—

5·241 thermal units = (a) heat used in raising the temperature of 1 cubic foot of air from 0° to 273° C., the volume remaining constant + (b) internal work done by or on the air in expanding from 1 cubic foot to 2 cubic feet + (c) external work in overcoming resistance equal to 2116·8 foot-pounds

Now, Mayer assumed that (b), the internal work done by or on the air in expanding, was *nil*. This is nearly true in the case of air; it is exactly true in the case of a perfect gas; but it is far from true in the case of many other gases.

If, for example, Mayer had based his reasoning on the behaviour of carbon dioxide under ordinary conditions, or on the behaviour of steam, his reasoning would have been yet less reliable. There is no reason given for the selection of air, and therefore his line of argument is not logical.

If, however, (b) were proved, then the method followed by Mayer can be used for determining the mechanical equivalent of heat from gases. The experiments on the subject are due to Joule and Thomson.

177. Joule's Experiments on the Internal Work of Expanding Gases.—Two strong vessels were connected by a narrow tube in which was a stop-cock. The stop-cock being closed, air was forced into one vessel until the pressure was 22 atmospheres; the air was exhausted from the other, and as perfect a vacuum as possible produced.

Both were placed in a vessel of water that formed a calori-

meter, so that both, together with the joining tubes, were entirely immersed. The water was kept thoroughly stirred, and the temperature read from delicate thermometers. When the temperature was constant, the stop-cock was turned; the air rushed into the vacuum and expanded to twice its volume, and, as it overcame no resistance, it did no external work. No change could be detected in the thermometers, and Joule concluded that, when air expands without doing external work, there is, on the whole, neither gain nor loss of heat; that is, that there is no internal work done in expanding the gas, otherwise the energy necessary must have been taken from the heat-energy of the gas, with a consequent fall in temperature.

There might, however, be a loss or gain of heat in one vessel, and an equal gain or loss of heat in the other, and to test this the experiment was modified. Each vessel was placed in a separate calorimeter. In one vessel (A) the air was again compressed; in the other (B) the vacuum was produced. The water in each calorimeter was well stirred, and the temperature noted. On turning the stop-cock the air rushed from A to B, and a slight diminution in temperature was observed in A's calorimeter, and a slight rise in temperature in B's calorimeter. With the usual precautions the loss of heat in A and the gain of heat in B were calculated, and these quantities were found to be equal.

The particles, in rushing from A to B, needed energy to give them the necessary motion. This energy was taken from the heat of A, with a consequent fall of temperature. The velocity of the particles was retarded again in B. A certain amount of momentum was destroyed, the result being the generation of heat, and the temperature of B rose.

Joule now came to the general conclusion that, if air expands without doing external work, there is, on the whole, neither rise nor fall in temperature, and that there is neither gain nor loss of energy in internal work.

Certain theoretical considerations showed, however, that, save in the case of a perfect gas rigorously obeying Boyle's law, the loss of heat in one case was not exactly equal to

the gain in the other, and that the internal work could be measured, if more delicate experiments were devised. This led to the following arrangement.

178. Joule's and Thomson's Experiments.—The object of the research is stated by the experimenters in the following terms ¹ :—

“Let air be forced continuously, and as uniformly as possible, by means of a forcing-pump, through a long tube, open to the atmosphere at the far end, and nearly stopped in one place so as to leave, for a short space, only an extremely narrow passage, on each side of which, and in every other part of the tube, the passage is comparatively very wide; and let us suppose, first, that the air, in rushing through the narrow passage, is not allowed to gain any heat from, nor (if it had any tendency to do so) to part with any to, the surrounding matter. Then, if Mayer's hypothesis were true, the air, after leaving the narrow passage, would have exactly the same temperature as it had before reaching it. If, on the contrary, the air experiences either a cooling or a heating effect in the circumstances, we may infer that the heat produced by the fluid friction in the rapids, or, which is the same, the thermal equivalent of the work done by the air in expanding from its state of high pressure on one side of the narrow passage to the state of atmospheric pressure which it has after passing the rapids, is in one case less, and the other more, than sufficient to compensate the cold due to the expansion; and the hypothesis in question would be disproved.”

Experiments were first conducted in which the air passed through a single orifice; but it was found difficult to determine the exact temperature of the issuing air—its temperature varied with the distance from the orifice, part of the energy was also used in imparting kinetic energy to the particles of air, and in starting sound-waves due to the air rushing through the orifice.

“The porous plug was adopted instead of a single orifice, in order that the work done by the expanding fluid might be immediately spent in friction, without any appreciable portion

¹ *Phil. Mag.*, 1852. Reprinted in Thomson's and in Joule's scientific papers.

of it being even temporarily employed to generate ordinary *vis-viva*, or being devoted to produce sound. The unconducting material was chosen to diminish as much as possible all loss of thermal effect by conduction, either from the air on one side to the air on the other side of the plug, or between the plug and the surrounding matter."

A long tube (Fig. 122) has a diaphragm, B C L M, of cotton wool, the tube is surrounded by another, R S T U, containing cotton wool or some other bad conductor, to prevent any heat entering or leaving the internal tube. The air before entering this protected part of the tube passes through a copper spiral 76 feet long. The spiral is surrounded by water kept well stirred, whose temperature is read carefully from thermometers openly divided. Thus the temperature of the air when it meets the diaphragm is known. A very delicate thermometer is placed beyond B C to determine the temperature of the air after it passes through the diaphragm.

The air is forced through the tube by a piston moving uniformly with a constant pressure, P (for convenience the piston P is shown in the figure; it would be placed, of course, in a part of the tube beyond the spiral), care being taken that the piston moves uniformly—and that there is therefore no increase in kinetic energy—and that there is therefore no loss of energy due to sound-waves caused by the air whirling through the diaphragm. A steady flow of air passes through the tube, so that equal masses will cross any section of the tube in equal times. The pressure beyond the diaphragm is that of the atmosphere, P'.

We are noting, not the effect of a sudden push of the piston, but of a continuous uniform movement of the piston, that may continue as long as we please. This gives the arrangement one marked advantage over that in § 177.

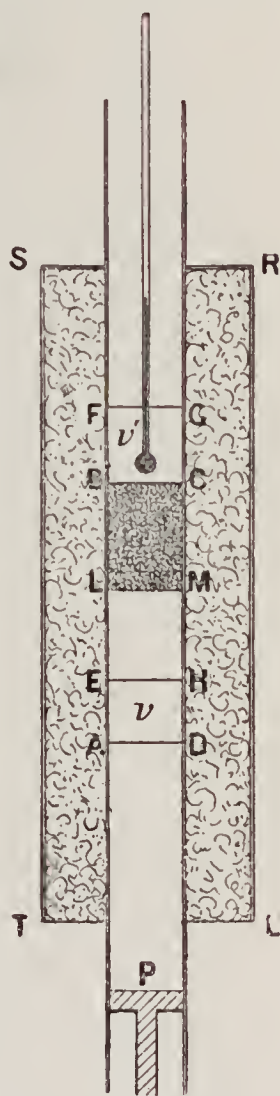


FIG. 122.

In the case of air it was found that the temperature was lower after flowing through the diaphragm; the lowering varied with the differences in pressure. Thus when the pressures differed by 1 atmosphere, the temperature fell 0.26°C . If the difference was 2 atmospheres, the fall in temperature was 0.52° .

Or if d = the fall in temperature in $^{\circ}\text{C}$;

P = the pressure of the air before entering the plug;

P' = atmospheric pressure on the other side of the plug,
both in atmospheres;

$$\frac{d}{P - P'} = 0.26^{\circ}\text{C. for air}$$

The results of the experiments show, for air and similarly for many other gases (hydrogen is an exception), that the heat of friction in the porous plug, which is the thermal equivalent of the work done by the air as it expands, is insufficient to compensate for the heat required to produce expansion, and there is a consequent fall in temperature.

If the pressure on the piston be but slightly above 1 atmosphere, the internal work in the case of air is only about $\frac{1}{500}$ of the work done in forcing the air through the plug.

In the case of carbonic acid gas the cooling is 1.151° for a difference of 1 atmosphere at 20°C .; at 91.5° it is only 0.703° per atmosphere. That is, the internal work becomes less as the gas is raised above its critical point.

Hydrogen is an exception. There is a slight rise in temperature after it expands. The internal work is negative.

With a small difference of pressure it is $\frac{1}{1250}$ of the external work.

Thus we see that air, hydrogen, and similar gases may, at ordinary temperatures, and with small variations in pressure, be treated as if they were perfect gases, that is, that the internal work done by the gas in expanding freely is practically *nil*. The same can be said of gases like carbonic acid gas and sulphur dioxide, provided their temperature is sufficiently high.

The series of experiments proved conclusively that if a gas be compressed, the work done in compression is not exactly equivalent to the heat produced by the compression, but that the internal work may be a positive or negative quantity, or may be *nil*, according to the gas experimented upon, and that therefore no assumptions must be made as was done by Mayer.

With definite knowledge derived from experiment of the internal work of air and other gases in expansion, and recognizing that it is so small in certain gases as to be negligible in first approximations, we can safely apply Mayer's method in determining the mechanical equivalent of heat.

179. Determination of the Internal Work of Expansion.—Collecting data from experimental results, we obtain the following:—

Let V (A D E H) and V' (B C F' G) represent the volume of 1 lb. of air before and after expansion (Fig. 122); use the other letters P, P' as explained above.

Let P and P' represent the pressure in pounds per square foot.

PV = the work done by the piston in forcing the air up to the plug (see § 186).

P'V' = work done by the air against the atmosphere (see p. 60).

If W = total work done in expansion in foot-pounds—

$$W - (P'V' - PV) = \text{work spent in friction in the plug (F)}$$

$$= \frac{W - (P'V' - PV)}{J} \text{ in heat-units } (J = 1390)$$

because the total work has its thermal equivalent (a) in the heat of friction in the plug (call this F), together with (b) the excess of the work done by the air against the atmosphere, over the work done in forcing the air up to the plug.

Let H = the actual heat necessary to compensate for the cold of expansion.

Heat of friction in the plug (F) = H, minus the heat that must be supplied to keep the gas, after expansion, at the same temperature as the gas before expansion (h)

For 1 lb. of air, $h = 1 \times$ specific heat of air at constant pressure (C) $\times d$

$$d = 0.26(P - P') \div \Pi \quad (\Pi = 1 \text{ atmosphere} = 2117 \text{ lbs. per square foot})$$

$$\therefore \frac{W - (P'V' - PV)}{J} = F = H - 0.26C \frac{P - P'}{\Pi}$$

$$\therefore H = \frac{W}{J} + 0.26C \frac{P - P'}{\Pi} - \frac{P'V' - PV}{J}$$

Regnault has shown that near the freezing point $\frac{P'V' - PV}{PV} = f \frac{P - P'}{\Pi}$ approximately, where $f = 0.00082$ for air, 0.0064 for carbonic acid, and -0.00043 for hydrogen; accepting this as being approximately true at 15°C. , and substituting, we have—

$$\begin{aligned} H &= \frac{W}{J} + 0.26C \frac{P - P'}{\Pi} - f \frac{PV}{J} \cdot \frac{P - P'}{\Pi} \\ &= \frac{W}{J} + \frac{PV}{J} \left(\frac{0.26CJ}{PV} - f \right) \frac{P - P'}{\Pi} \end{aligned}$$

For air, $CJ = 0.2375 \times 1390 = 330$.

The volume of 1 lb. of dry air at $0^\circ \text{C.} = 12.39$ cubic feet.

$$\begin{aligned} \therefore \text{at } 15^\circ \text{C.}, PV &= 2117 \times 12.39(1 + 15 \times 0.003665) \\ &= 27671 \end{aligned}$$

$$\therefore H = \frac{W}{J} + \frac{PV}{J} \cdot \frac{P - P'}{\Pi} \times 0.0023$$

For carbonic acid, with analogous substitutions, the 0.0023 is 0.013 ; while for hydrogen it is -0.0008 .

The total work done when a gas represented by (PV) expands to $(P'V')$

$$= PV \log_e \frac{P}{P'} (\S 186) = PV \frac{P - P'}{\Pi} \text{ nearly}$$

if the difference between P' and P be small.

Therefore the ratio of the excess of the actual heat needed in expansion over the thermal equivalent of the work done in expansion equals—

$$\begin{aligned}
 r &= \frac{H - \frac{W}{J}}{\frac{W}{J}} = \frac{PV}{J} \cdot \frac{P - P'}{\Pi} \times 0.00023 \div \frac{PV}{J} \cdot \frac{P - P'}{\Pi} \\
 &= 0.0023 \\
 r &= 0.0023 \text{ for air} = \frac{1}{420}
 \end{aligned}$$

Therefore if we subject atmospheric air to a pressure slightly above 1 atmosphere, at ordinary temperatures, and if W be the work done in compression, the heat evolved is mechanically equal to—

$$W + \frac{W}{420}$$

If carbon dioxide be experimented upon under similar conditions—

$$r = 0.013 = \frac{1}{77}$$

The heat evolved would be mechanically equal to $W + \frac{W}{77}$

In the case of hydrogen, the heat evolved would be mechanically equal to $W - \frac{W}{1250}$

180. Determination of the Mechanical Equivalent of Heat from Hydrogen.—(1) Assume, what is practically true, that hydrogen in expanding behaves like a perfect gas, that there is no internal work done by it or upon it when it expands freely. (Mayer's hypothesis.)

(2) Facts collected from experiments.

(a) 1 gram of hydrogen at 0° C. and under a pressure of 760 mm. of mercury, measures 11,164.45 c.c.

(b) The pressure due to a height of 760 mm. of mercury is 1033.3 grams per square centimetre in the latitude of London.

(c) The specific heat of hydrogen at constant pressure (C) is 3.409; the specific heat at constant volume (c), as determined from the velocity of sound, is $3.409 \div 1.41$, because $\frac{C}{c} = 1.41$.

Let us experiment upon 1 kilogram of hydrogen at 0°C . and 760 mm. pressure. Its volume will be 11.16445 cubic metres. Take as the unit of heat the heat required to raise the temperature of 1 kilogram of water 1°C .

Enclose the hydrogen in a cylinder, as in § 176, whose section is 1.116445 square metre, then the gas will stand 10 metres high in the cylinder. The pressure on the piston will be 10333×1.116445 kilogram = 11536.2 kilograms.

(1) Allowing the gas to expand at constant pressure, apply heat until its temperature rises 1° . This will require a number of units of heat numerically equal to the specific heat at constant pressure (C). The piston will rise $\frac{10}{273}$ metre,

and do $\frac{10}{273} \times 11536.2$ kilogrammetres of work = 422.6 kilogrammetres of work.

(2) Beginning with the gas at its original volume, temperature, and pressure, keep the piston fixed, and apply heat to raise the temperature 1° . This will require c units of heat. c = specific heat of hydrogen at constant volume.

Heat-units.	Dynamical result.		
		Internal work.	External work.
C	Temperature of 1 kilogram raised 1°	Practically <i>nil</i> from Joule's and Thomson's experiments	422.6 kilogrammetres
c	Temperature of 1 kilogram raised 1°	<i>Nil</i>	<i>Nil</i>

$\therefore C - c$ is equivalent to 422.6 kilogrammetres of work

$$\text{also } c = \frac{C}{1.41}$$

$\therefore C$ is equivalent to $422.6 \times \frac{1.41}{0.41}$ kilogrammetres

∴ if J be the mechanical equivalent of 1 unit of heat—

$$J = \frac{422.6 \times 1.41}{0.41 \times 3.409} \\ = 426.2 \text{ kilogrammetres of work}$$

The student should notice that the specific heat at constant volume (c) is determined from the specific heat at constant pressure (C) by the relation—

$$\frac{C}{c} = 1.41$$

This ratio is frequently calculated from relations involving the mechanical equivalent of heat. Evidently c calculated in this way is inadmissible in any determination of the mechanical equivalent of heat. C and c must either be determined separately or $\frac{C}{c}$ be determined by some independent method, such as the method based on the velocity of sound (§ 183).

181. General Case, assuming Mayer's Hypothesis.—Let V , P , T represent the volume, pressure, and absolute temperature of a perfect gas whose mass is 1 gram.

(1) Let the mass be heated to a temperature T' , expanding at constant pressure P .

(a) It must be supplied with $C(T' - T)$ thermal units.

(b) The new volume V' becomes $V \cdot \frac{T'}{T}$ ($\because \frac{PV}{T} = \frac{PV'}{T'}$)

$$\therefore \text{the increase in volume} = V \cdot \left(\frac{T' - T}{T} \right)$$

$$\text{And the external work done} = PV \cdot \frac{T' - T}{T}$$

(2) Without work being done upon it, let the volume V' change to V , the temperature remaining at T' , the pressure will change so that the new pressure $P' = P \cdot \frac{V'}{V}$

$$\left(\frac{PV'}{T'} = \frac{P'V}{T'} \right)$$

(3) Let heat escape until the pressure becomes P . The

volume being V , the temperature must be T ; the gas is losing heat at constant volume.

\therefore it loses $c(T' - T)$ units

The gas is now in its original condition. It has received $C(T' - T)$ and lost $c(T' - T)$ units of heat, and has done $PV \cdot \frac{T' - T}{T}$ units of external work.

$\therefore (C - c)(T' - T)$ units of heat are equivalent to $PV \cdot \frac{T' - T}{T}$ units of work

If, therefore, J is the mechanical equivalent of heat—

$$J = \frac{1}{C - c} \cdot \frac{PV}{T}$$

$$\frac{PV}{T} = \frac{P_0 V_0}{T_0} \text{ and if } \frac{C}{c} = k, C - c = C\left(1 - \frac{1}{k}\right) = C \frac{k - 1}{k}$$

$$\begin{aligned} \therefore J &= \frac{k}{k - 1} \cdot \frac{1}{C} \cdot \frac{P_0 V_0}{T_0} \\ &= \frac{k}{k - 1} \cdot \frac{1}{C} \cdot \frac{P_0 V_0}{273} \end{aligned}$$

k for gases that are nearly perfect is 1.41; P_0 is the pressure due to 760 mm. of mercury, *i.e.* a pressure of 1033.3 grams per square centimetre. V_0 , the volume of 1 gram of the gas at 0° C. and 760 mm. pressure, equals $\frac{1}{D_0}$, where D_0 is the density under the same conditions.

$$\begin{aligned} J &= \frac{1.41}{0.41} \cdot \frac{1033.3}{273} \cdot \frac{1}{CD_0} \\ &= 13.02 \frac{1}{CD_0} \end{aligned}$$

The units are the gram, centimetre, degree Centigrade. To change into the usual units—kilogram, metre, degree Centigrade—we must multiply by $\frac{1000}{1000 \times 100}$

$$\therefore J = 0.1302 \frac{1}{CD_0}$$

∴ if we take D as the mass of 1 cubic metre, then—

$$J = 130200 \cdot \frac{1}{CD_0}$$

For air, $C = 0.2375$; $D_0 = 1293$.

∴ $J = 423.9$ kilogrammetres of work

For oxygen, $C = 0.2175$; $D_0 = 1429.8$.

$$\therefore J = 420$$

The determination is not so near as the above, but for oxygen $k = 1.403$. With this correction $J = 425$.

For nitrogen, $C = 0.2438$; $D = 1256$.

$$\therefore J = 425$$

182. The Difference in Thermal Units of the Two Specific Heats.—Returning to the formula where $C - c$ is equivalent to $\frac{PV}{T}$, and noting that—

$$\frac{PV}{T} = \frac{P_0V_0}{T_0} = \text{constant } R$$

we have $C - c = R$.

This enables us to determine the difference between the two specific heats.

It is only necessary to determine R under the most convenient conditions.

For example, for air at 0° C. and 760 mm. pressure as before—

$$\frac{P_0V_0}{T_0} = 2927$$

The thermal equivalent will be $\frac{2927}{J} = \frac{2927}{42400} = 0.0691$

$$\therefore C - c = 0.0691$$

Regnault found experimentally that $C = 0.2375$.

$$\therefore \frac{C}{c} = \frac{C}{C - R} = \frac{0.2375}{0.2375 - 0.0691} = 1.41$$

183. Ratio of the Specific Heats deduced from the Velocity of Sound.—Newton concluded from mathematical

investigations that the velocity of sound could be calculated from the formula—

$$v = \sqrt{\frac{E}{D}}$$

where v = velocity, E = elasticity, and D = density. In air or other gas at constant temperature, the elasticity is equal to the pressure P .

$$\therefore v = \sqrt{\frac{P}{D}}$$

At 0° C. and 760 mm. pressure, the pressure is equal to 1033.3 grams per square centimetre. The accelerative force of gravity = 981 centimetres per second per second.

$$\therefore E = P = 1033.3 \times 981 = 1013667$$

D = density = 0.001293 gram per cubic centimetre.

$$\therefore v = \sqrt{\frac{1013667}{0.001293}} = 28,000 \text{ centimetres per second nearly}$$

Actual experiment makes the speed about 33,000 centimetres per second. Such a difference between *calculation* and *fact* showed that some error had been committed in the calculation.

Newton, in his calculation, allowed for the fact that, when a gas is compressed, its elasticity is increased because its density is increased. If we compress a gas very slowly, so that the heat is allowed to escape, the temperature does not rise, and this increase of elasticity, due to increase of density, is the only increase to allow for. But by the fire-syringe experiment it is seen that, if the gas be compressed suddenly, heat is evolved, and this heat increases the elasticity—that is, an increased pressure must be applied to keep its volume constant. Similarly, if a gas be suddenly rarefied, the gas is cooled, and this lowering of temperature lessens the elasticity, and therefore the question cannot be considered as if the temperature remained constant, that is, we cannot assume that $E = P$.

What takes place when sound travels in air? The particles are suddenly compressed at the condensed part of the wave, and are therefore heated. The particles are suddenly separated

at the rarefied part of the wave, and are cooled as much as they were heated at the condensed part; therefore the *average* temperature remains the same. The condensed particles are heated, their elasticity is increased; they therefore tend the more to separate, they separate the more rapidly, and thus the speed of the wave is increased. Condensation is succeeded by rarefaction, and the rarefied part is cooled. Its elasticity is reduced; therefore the condensed particles are the more easily able to rebound, and again the speed of the wave is increased.

The condensation and rarefaction take place so rapidly that heat has not time to escape by conduction.

Taking these facts into account, Laplace showed that the formula for the velocity must express the elasticity under the conditions, and that the corrected formula was—

$$v = \sqrt{\frac{C}{c} \cdot \frac{P}{D}}$$

—a formula that includes the ratio of the two specific heats.

$$\frac{C}{c} = v^2 \cdot \frac{D}{P}$$

v , D , and P can be measured, and therefore the ratio $\frac{C}{c}$ can be determined.

The ratio is found to be equal to 1.41 (§ 66).

184. Adiabatic Lines.—The relation between the volume (v) and pressure (p) of a perfect gas while the temperature remains constant is—

$$pv = \text{a constant}$$

$$\text{or } pv = RT$$

where T is the absolute temperature. This relation is represented graphically by an isothermal line, the curve being a rectangular hyperbola (§ 42).

The formula is only approximately true in experiments if the variation in volume takes place slowly, so that the heat, the result of compression, has time to escape. In many operations we approximate to a condition in which the *heat-*

energy cannot enter or escape from the apparatus, as, for example, when we compress or allow a gas to expand suddenly, or when we compress or allow a gas to expand in a vessel whose sides are bad conductors. There is in such experiments a rise or fall in temperature (§ 183).

Let A (Fig. 123) represent the relation between volume, pressure, and temperature of a given mass of a gas at any

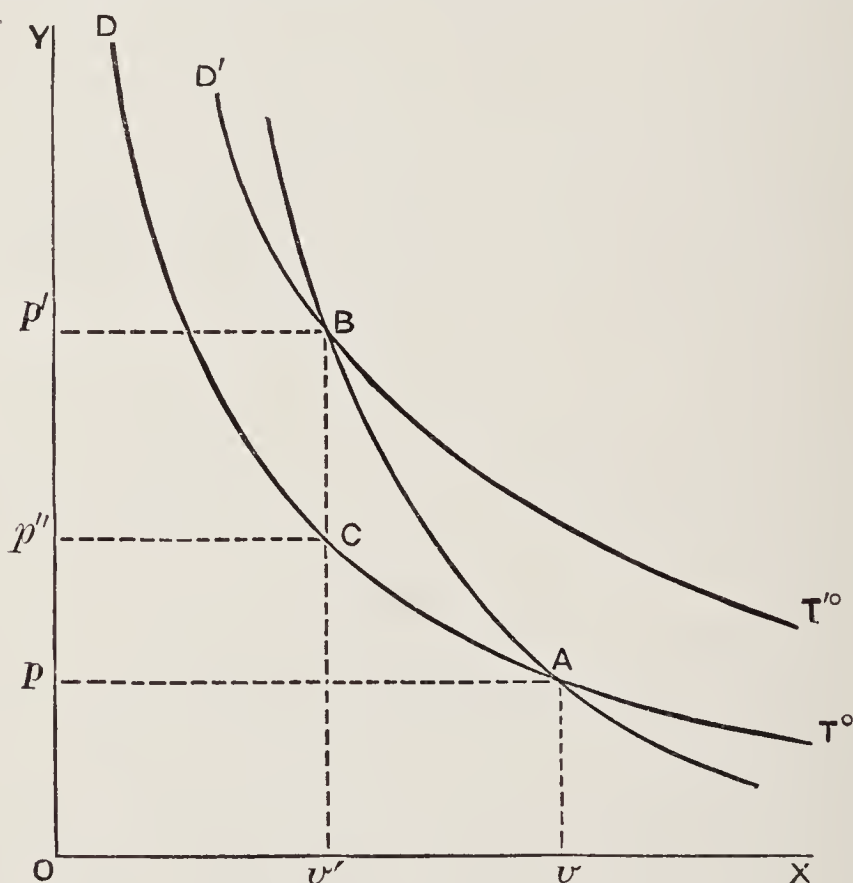


FIG. 123.

given time, the volume being Ov , the pressure vA or Op , and the temperature T . $TACD$ is the isothermal for the given mass of the gas for T^0 ; $T'BD'$ is the isothermal for the same gas at some higher temperature, T'^0 .

If the pressure be increased, so that heat cannot escape, the temperature generally will rise, and there will be increased resistance to compression, so that a greater increase in pressure will be required to effect a given decrease in volume than would be the case if the heat generated were allowed to escape. Thus if we take the gas when the absolute temperature is T'^0 and the volume Ov' , the pressure Op' or $v'B$ will be greater than

$O p''$ or $v' C$, the pressure corresponding with the volume $O v'$ when the temperature remains constant.

This reasoning will apply, however small the difference between T° and T'° . The new curve, AB , called an adiabatic curve, expresses the relation between the volume and pressure of a gas when no heat is allowed to enter or escape; when it crosses an isothermal curve, it makes a greater angle with the line of volumes than does the isothermal curve (Fig. 124).

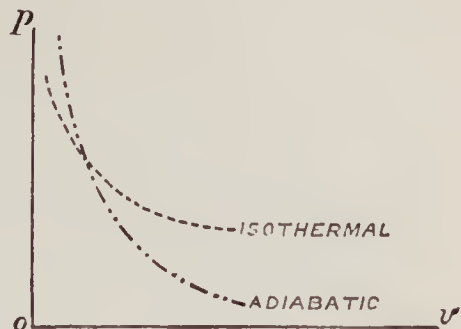


FIG. 124.

In the isothermal lines the temperature is constant; in the adiabatic lines there is also a quantity that is constant; this will be dealt with in § 196.

In the above we have discussed the adiabatic curve with respect to a substance that remains in the gaseous condition. The line can be drawn equally well for liquids and solids, save that as in the case of the isothermals the diminution of volume is so small compared with the increase in pressure, that it is not easy to represent the variation on a diagram.

The adiabatic for a mixture of vapour and liquid is im-

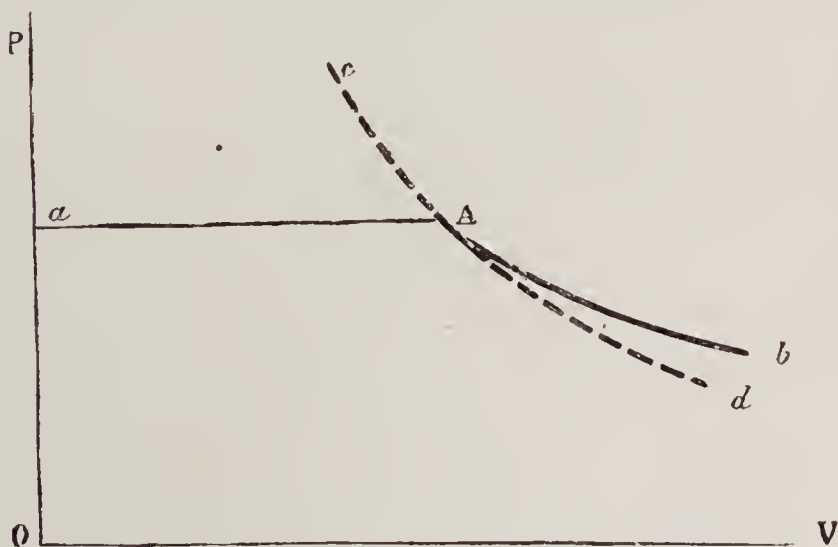


FIG. 125.

portant. Let us take the best known case of steam and water.

Let the position A (Fig. 125) represent the volume and pressure of 1 lb. of steam at 212°F . From Regnault's tables

we know that the pressure will be 14.7 lbs. per square inch, and the volume will be 26.36 cubic feet. So that on the diagram $OA = 26.36$, and $OA = 14.7$.

(1) If we keep the temperature constant and attempt to decrease the volume, we find that the pressure remains constant, part of the steam condenses; in fact, we describe the isothermal Aa for steam in the presence of its liquid, and during the process part of the heat must escape. If from A we keep the temperature constant and increase the volume, then the steam remains a vapour, acts nearly like a gas, and the part of the isothermal, Ab , is described.

(2) If the 1 lb. of steam be in a cylinder closed with a piston, all impervious to the flow of heat, then, if the pressure be increased, the temperature of the steam will rise, and allow it still to exist as steam at the higher pressure. For example, if the temperature rises to 213°F ., the steam will remain as a vapour provided that the pressure is 14.99 lbs. per square inch; with a temperature of 215° the steam will only begin to condense if the pressure be more than 15.6 lbs. on the square inch. The actual pressure in this experiment is not sufficient to produce condensation, and thus the adiabatic line is a curve, Ac . It can also be shown that, if the steam be in contact with water at the same temperature, increase in the pressure produces sufficient heat not only to allow the steam to exist as steam, but to evaporate part of the water.

Returning to the point A , let the volume increase, heat being prevented from entering or leaving the substance. The steam, expanding, moves the piston and does work. There is a consequent fall in the temperature; the fall is so great that when the pressure is say 14 lbs. on the square inch, the temperature to keep all as steam should be 209°F .; it is, however, lower than this, so that part of the steam condenses, the liberation of heat keeping the remainder dry and saturated. For any given pressure the volume will be less than it would be for an isothermal; the adiabatic curve, Ad , will fall below the isothermal Ab .

bAa is the isothermal for steam at 212°F .

dAc is the adiabatic curve for steam passing through A ;

the point A represents the condition that the temperature is 212° F., the pressure 14.7 lbs. per square inch, and the volume 26.36 cubic feet.

The isothermal curve for a perfect gas is a rectangular hyperbola, whose equation is—

$$pv = \text{a constant}$$

$$\text{or } pv = RT$$

where T is the absolute temperature.

The value of R is determined from one observation. For example, in the case of 1 lb. of air at 0° C. and at normal pressure (2116.8 lbs. per square foot), the volume is 12.39 cubic feet, and the constant is—

$$R = \frac{pv}{T} = \frac{2116.8 \times 12.39}{273} = 96$$

In an adiabatic curve increase of volume is accompanied by greater decrease of pressure than would be the case along any isothermal passing through the same point.

It can be shown that generally the relation between pressure and volume along an adiabatic curve can be expressed by—

$$pv^n = \text{constant}$$

For a perfect gas $n = \frac{C}{c} = 1.41$ (§ 183); that is—

$$pv^{1.41} = \text{a constant}$$

For dry steam an approximate formula is $pv^{\frac{17}{16}} = \text{a constant}$.

185. Work done by a Gas in Expanding.—If a gas be subjected to a given uniform pressure, as, for example, that of the atmosphere, then, if the gas expands, it does work against this pressure. The measure of the work done will be the pressure into the distance moved. In the case of a cubic foot of gas at atmospheric pressure, let it expand to $1\frac{1}{2}$ cubic foot; then the increase in volume is $\frac{1}{2}$ cubic foot. If the movable piston be $\frac{1}{2}$ square foot in area, it will move 1 foot.

The pressure on 1 square foot = $14.7 \times 144 = 2116.8$ pounds

$$,, \quad ,, \quad \frac{1}{2} \quad ,, \quad = 2116.8 \times \frac{1}{2}$$

$$\text{Work done} = (2116.8 \times \frac{1}{2}) \times 1 \text{ foot-pounds}$$

$$,, \quad = 2116.8 \times (\frac{1}{2} \times 1) \quad ,,$$

$\frac{1}{2} \times 1$ is the increase in volume, so that work done = pressure \times increase in volume.

Generally, if the pressure be P per unit area, and the area of the piston be A , the total pressure is PA , if the distance moved be x .

$$\text{Work done is } PAx = P \times Ax = Pv$$

where v is the increase in volume.

186. Indicator Diagram.—Graphic Representation of Work done.—Let Oa (Fig. 127) represent a volume, aA a pressure, according to a definite scale.

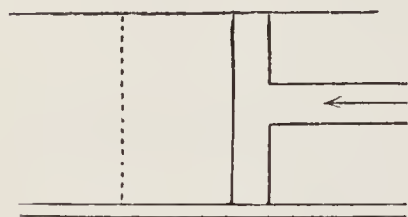


FIG. 126.

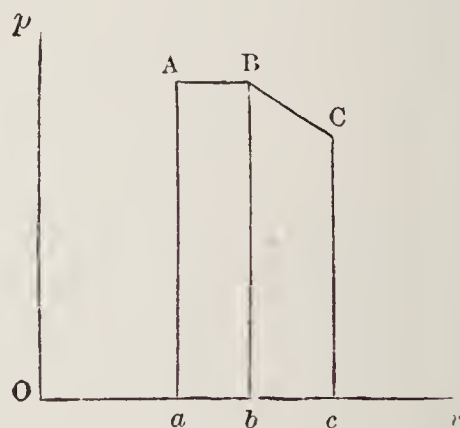


FIG. 127.

Let the gas expand from Oa to Ob , the pressure remaining uniform; that is, the line AB will be horizontal.

$$\begin{aligned} \text{The work done} &= \text{pressure} \times \text{increase in volume} \\ &= aA \times (Ob - Oa) \\ &= aA \times ab \\ &= \text{area } aABb \end{aligned}$$

If the pressure increases or decreases uniformly, it is still easy to estimate the work done. Let the initial pressure and volume be Bb , Ob . Let the volume increase to Oc while the pressure decreases uniformly to Cc , so that BC is a straight line. As the pressure has changed uniformly, we can take the average pressure

$$\begin{aligned} &= \frac{1}{2}(Bb + Cc) \\ \text{Work done} &= P \times \text{increase in volume} \\ &= \frac{1}{2}(Bb + Cc)(bc) \\ &= \text{area } bBCc \end{aligned}$$

Generally the line is a curve, A B (Fig. 128). We then estimate the work done in expanding from O a to O b by dividing a b into a very large number of equal parts, and drawing the verticals c m, d n, etc.

If $ac = cd \dots$ be very small, no appreciable error will be made by calling A m, m n, \dots straight lines. The work done will then be the areas $aAmc$, $cmnd$, \dots or the total work the area of the figure a A B b.

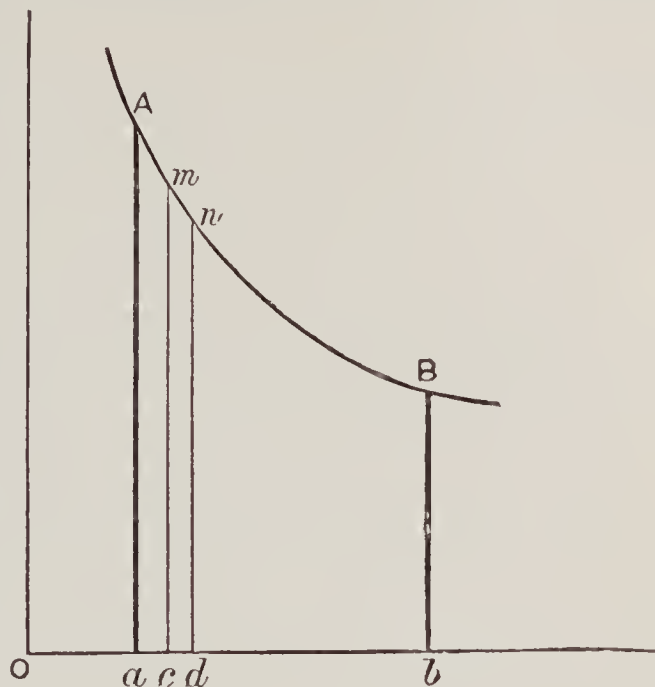


FIG. 128.

The estimation of such areas belongs to pure mathematics, and it can generally be done if the form of the curve A B is known.

The two curves of most frequent use in heat are $p v = \text{constant}$, and $p v^n = \text{constant}$.

(1) *Area of a A B b when $p v = \text{constant}$.*

If the point A represents $p_1 v_1$, while B represents $p_2 v_2$ —

$$\begin{aligned} \text{The area } aABb &= Aa \times Oa \times \log_e \frac{Ob}{Oa} \\ \text{or} &= Bb \times Ob \times \log_e \frac{Ob}{Oa} \end{aligned}$$

That is—

$$\text{Work done} = p_1 v_1 \log_e \frac{v_2}{v_1} = p_2 v_2 \log_e \frac{v_2}{v_1}$$

$$p_1 v_1 = p_2 v_2 = RT$$

(T is absolute temperature)

$$\therefore \text{work done} = p_1 v_1 \log_e \frac{v_2}{v_1} = RT \log_e \frac{v_2}{v_1}$$

(2) *Area of a A B b when $p v^n = \text{constant}$.*

$$\text{Area} = \frac{Aa \times Oa - Bb \times Ob}{n - 1}$$

$$\therefore \text{work done} = \frac{p_1 v_1 - p_2 v_2}{n - 1}$$

A frequent value of n is $\frac{C}{c} = 1.41$.

$$\therefore \text{work done} = \frac{p_1 v_1 - p_2 v_2}{0.41}$$

By the aid of an indicator diagram we can estimate the work done by or on a working substance (*a*) by calculating, if the curve be a known curve; or (*b*) by measuring the area.

Attached to steam-engines is an apparatus that registers automatically the variations in volume and pressure.

Let *A* be the starting-point, and let the curve traced be *A B C D E*. From *A* to *C* the working substance does work, whose measure is the area *a A B C c*. From *C* to *E* work is

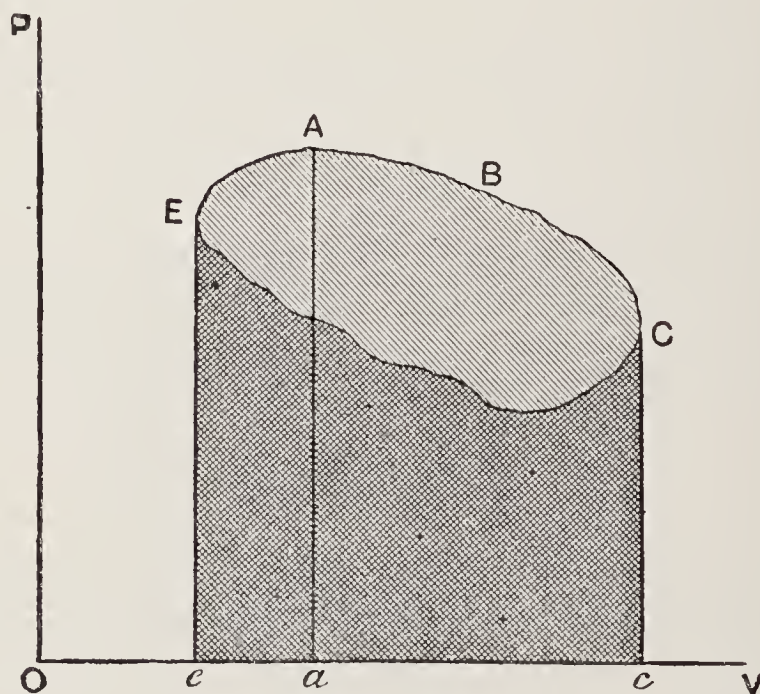


FIG. 129.

done on the substance; its measure is *c C E e*; from *E* to *A* the substance does work, whose measure is *e E A a*.

$$\text{Work done by} = e E A a + a A B C c$$

$$,, \text{ upon} = c C E e$$

$$\therefore \text{nett work done} = A B C E A$$

Returning to the point A means that the working substance is again in exactly the same physical condition as at starting.

In many operations this condition, that the working substance is brought into its original condition as regards volume, temperature, and pressure (only two need be defined), is not fulfilled, but in the discussion that follows this is always the case, so that the curve is closed.

187. A Cycle of Operations.—If a series of operations be performed upon a working substance, so that its final physical state is in all respects similar to its original state, the series of operations is called a cycle of operations.

For example, we may begin with a pound of steam at 212° F. Its pressure will be 14.7 lbs. on the square inch, while its volume will be 26.36 cubic feet. We may increase the pressure, preventing the escape of heat, when we shall form the adiabatic curve for steam, and the temperature will rise. Let the new pressure be 20 lbs. on the square inch. Then we may allow heat to escape until the temperature falls to 228° F. If a further reduction of temperature takes place with this pressure, some of the steam will condense. Imagine that the temperature sinks to 200° . All the steam will have condensed, and if the pressure remains at 20 lbs. on the square inch, the water will be compressed.

Now let heat be applied until the temperature is 212° F., the pressure remaining at 20 lbs. per square inch. Reduce the pressure to 14.7 lbs. on the square inch; the whole will evaporate, and its volume will be 26.36 cubic feet as before.

The final condition is exactly the same as the original condition, both as regards volume, pressure, and temperature. A cycle of operations has been performed.

Another example may be cited. Unit mass of air is taken at certain volume (v), temperature (t), and pressure (p).

(1) Heat is supplied, the volume remaining constant until the temperature rises to t'° and the pressure becomes p' (i.e. $c(t' - t)$ units of heat supplied).

(2) The mass is allowed to expand, doing work, until the pressure is again p , the temperature remaining t'° .

(3) Heat is taken away until the temperature falls to t° , the volume becoming again v ($C(t' - t)$ units taken away).

(4) The mass is now in the original condition (v, t, p).

A cycle of operations has been performed.

188. Carnot's Cycle.—Carnot, in 1824, described a theoretic heat-engine that has been of great service in the study of heat. Carnot believed in the then accepted idea that heat was a material substance, and in the modern statements his original method is altered to suit the dynamical theory. Carnot's memoir was neglected until its value was pointed out by Sir W. Thomson.

The engine.—An essential part of the engine is that the working substance may be any substance whatever. The results are independent of the substance; it may, for example, be air, steam, hydrogen, a liquid, a solid, or partly liquid and vapour, etc. It is convenient to take a gas, as the variations in volume are more marked; but this selection is a matter purely of convenience.

The substance D (Fig. 130) is contained in a cylinder so

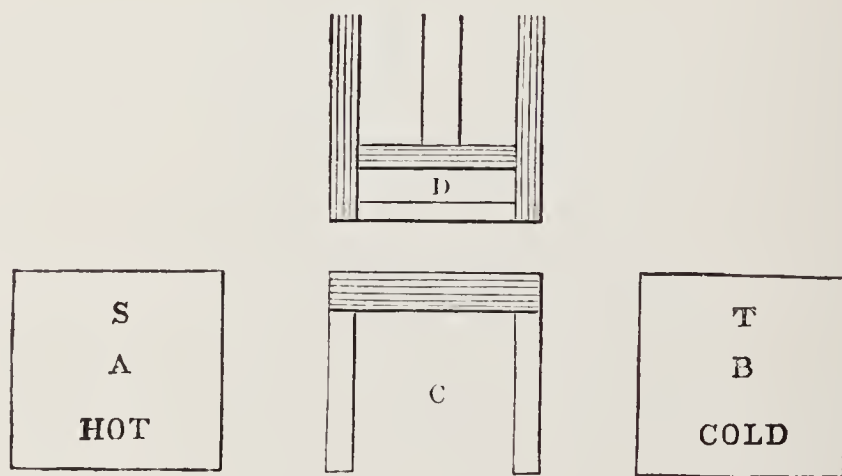


FIG. 130.

constructed that the sides and the piston are perfect non-conductors, so that no heat can enter or leave by them. The capacity for heat of the piston and sides is zero. The base of the cylinder is a perfect conductor.

The other parts are (1) a hot body, A, called the source, which is kept at a constant temperature, S; (2) a body, B,

colder than A, which is kept at a constant temperature, T , and which is called the refrigerator ; and (3) a stand, C, the upper surface of which is a perfect non-conductor, like the sides of the cylinder and the piston.

Let the cylinder be placed on A when the temperature of the working substance is S ; then, whatever motion of the piston takes place, since heat passes freely through the base, and the supply from S is inexhaustible, the relation between volume and pressure will always be expressed by

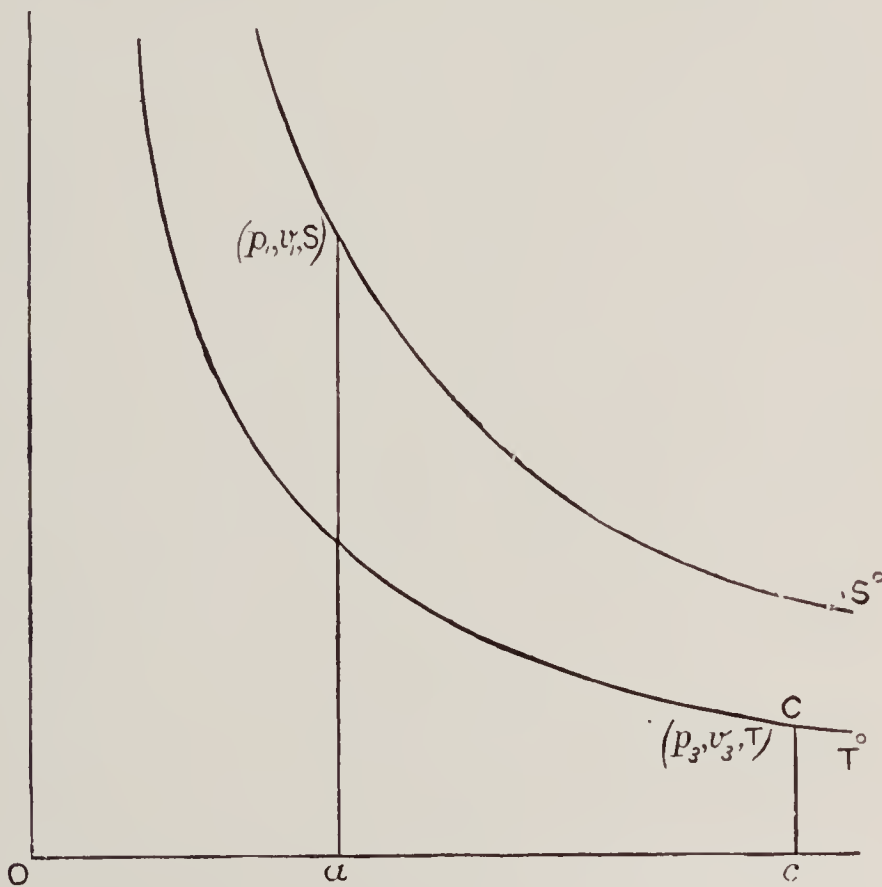


FIG. 131.

the isothermal of the substance for S degrees (curve AS , Fig. 131). The point A indicates the condition that the pressure (p_1) is Aa , the volume (v_1) Oa , and the temperature S .

If the cylinder be placed on B when the temperature of the working substance is T , then the relation between volume and pressure will always be expressed by the isothermal for T° .

The point C gives for the same mass, a volume (v_2) Oc ,

pressure $C_c (p_3)$, and temperature T (the student will note that no particular scale of temperature is defined).

If the cylinder be placed on the stand, then, as no heat can enter or escape, the relation between volume and pressure will be expressed by an adiabatic line; the particular line depending upon the original conditions of volume, temperature, and pressure (Fig. 132).

For the purpose we have in view the adiabatic curves pass

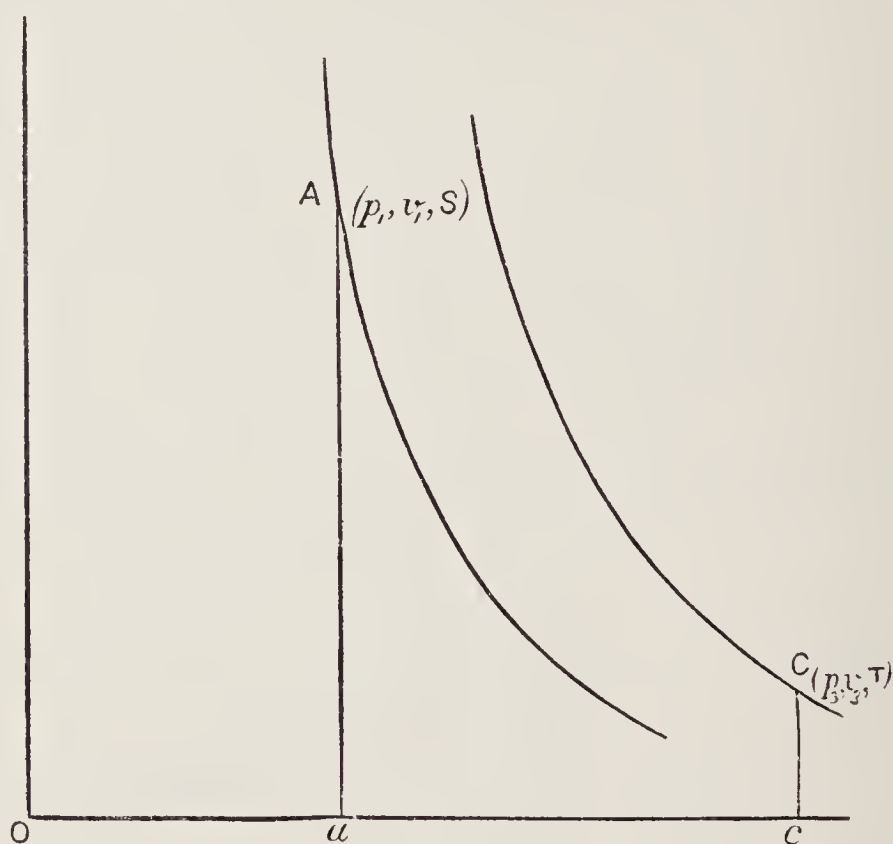


FIG. 132.

through the points A and C of Fig. 131, which, we have seen, represent the relation of pressure, volume, and temperature as described in the figure.

Let Fig. 131 be placed on Fig. 132. Then the points A and C coincide, also the adiabatics and isothermals intersect at B and D, and the value of volume and pressure can be calculated for these two positions (Fig. 133).

Suppose that for the given working substance the isothermals S and T have been carefully determined, also that the adiabatics passing through A and C have been determined; that

is, that by preliminary experiments, Fig. 133 has been mapped out. Furthermore, we may imagine that indicators register on this perfectly theoretical machine the pressure and volume, and also the quantities of heat taken in or given out at any period. Carnot's four operations can now be followed.

First operation.—Place the cylinder on the hot body A, and begin the operation when the pressure is p_1 , the volume v_1 , and the temperature S. This condition is indicated on the diagram by the point A (Fig. 133).

Now let the substance expand. Heat flows from S, keeping

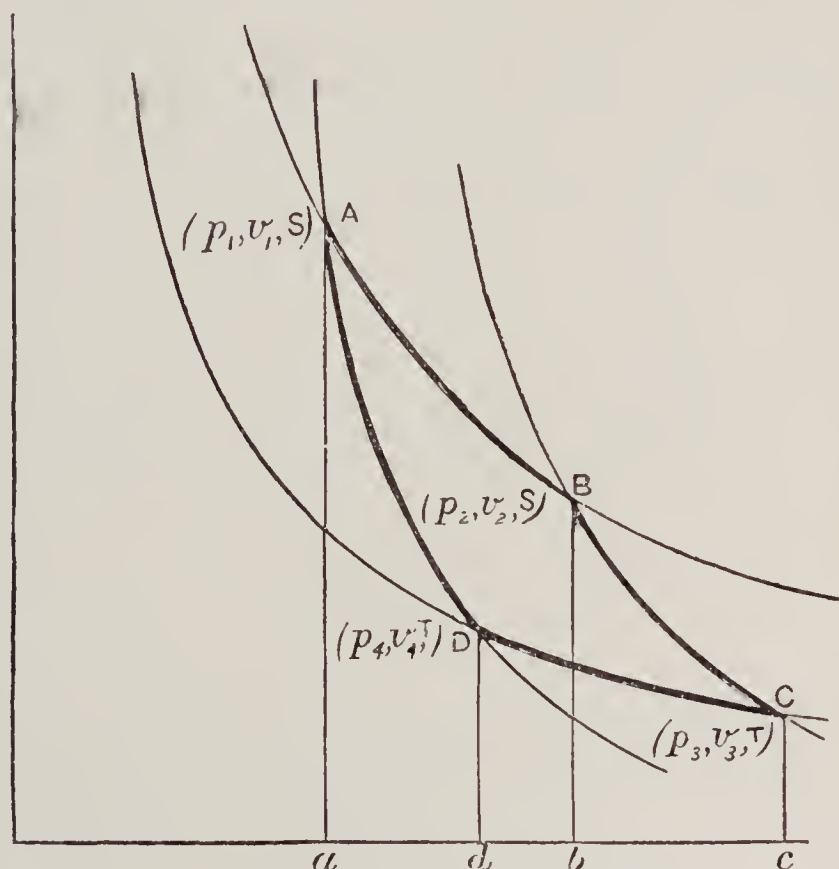


FIG. 133.

the temperature constant at S, therefore the isothermal curve A B is described. When the volume is $O b (v_2)$ and the pressure $b B (p_2)$, stop the operation. A quantity of heat, which we may call H, has entered the working substance.

Second operation.—Place the cylinder on the stand. Let the body continue to expand. It will do so adiabatically, and the relation between the pressure and volume will be represented

by the curve B C. The temperature gradually falls. When it reaches the temperature T, stop the operation, and place the cylinder on the cold body B. So far the working substance has been doing work by moving the piston against external pressure.

Third operation.—Begin to push back the cylinder, that is, do work on the working substance. Variation in temperature is impossible, seeing that heat readily escapes to B. The isothermal C D is described. When the position is reached expressed by D (volume v_4 , pressure p_4), stop the operation; that is, stop at a point selected so that the compression in the fourth operation will bring the substance back to its original conditions. A quantity of heat, h , has escaped from the working substance to B. Place the cylinder on the stand.

Fourth operation.—Continue to press back the cylinder. Heat is generated, the temperature rises, and the adiabatic curve D A is described. When the temperature T is reached, the position will be A; that is, the pressure is p_1 , the volume is v_1 , and the temperature is S.

The working substance is now exactly in the original condition. A cycle of operations has been performed.

The determination of the points A, B, C, D, is evidently possible.

Let us sum up what has been done.

(1) In the first and second operations a quantity of heat, H, has entered the working substance, and the amount of work done by the substance is measured by the areas A B $b a$, B C $c b$.

(2) In the third and fourth operations a quantity of heat, h , has been taken from the working substance, and the work done on the substance is measured by $c C D d$ and $d D A a$.

A quantity of heat, H, at temperature S, has been taken in, and a quantity, h , at temperature T, has been given out.

The excess of work done by the substance over the work done in it is—

$$ABCca - CcaAD$$

that is, the work measured by A B C D.

That is, a quantity of heat, $H - h$, is equivalent to a quantity of work that is measured by A B C D.

If H and h are measured in heat-units, and J is the mechanical equivalent of heat—

$$J(H - h) = \text{area } ABCD = W \text{ the useful work}$$

If, as is generally done, we express H or h in dynamical units (foot-pounds or foot-poundals)—

$$H - h = W$$

189. Illustration from a Perfect Gas.—If the working substance be a gas obeying Boyle's law, and we measure temperature from absolute zero on the Centigrade scale, we obtain the following:—

If A represent p_1v_1S ; B , p_2v_2S ; C , p_3v_3T ; D , p_4v_4T —

$$\text{Work done} = ABCD = ABba + BCcb - cCDd - dDAa$$

$$\begin{aligned} (\text{See § 186.}) \quad &= p_1v_1 \log_{\epsilon} \frac{v_2}{v_1} + \frac{p_2v_2 - p_3v_3}{n - 1} - p_3v_3 \log_{\epsilon} \frac{v_3}{v_4} \\ &\quad - \frac{p_1v_1 - p_4v_4}{n - 1} \end{aligned}$$

$$p_1v_1 = RS, \text{ etc.} \quad \text{Log}_{\epsilon} \frac{v_2}{v_1} = \log_{\epsilon} \frac{v_3}{v_4}$$

$$\begin{aligned} \therefore ABCD &= RS \log_{\epsilon} \frac{v_2}{v_1} - RT \log_{\epsilon} \frac{v_2}{v_1} + \frac{R}{n - 1} (S - T - S + T) \\ &= R \log_{\epsilon} \frac{v_2}{v_1} (S - T) = W \end{aligned}$$

The efficiency of a machine is the ratio of the work done to the heat supplied.

$$\frac{W}{H} = \frac{R \log_{\epsilon} \frac{v_2}{v_1} (S - T)}{R \log_{\epsilon} \frac{v_2}{v_1} \cdot S} = \frac{S - T}{S}$$

$H = R \log_{\epsilon} \frac{v_2}{v_1} \cdot S$; because it equals external work done, since the internal work is zero (§§ 178, 179).

For example, if S be 100°C. and T 0°C. —

$$\text{The efficiency} = \frac{374 - 274}{374} = \frac{100}{374}$$

With a given temperature of supply, S , we can only increase the efficiency by obtaining a lower temperature for the condenser.

The solution of the problem of obtaining increased efficiency lies in making $\frac{S - T}{S}$ as nearly as possible equal to unity; that is, in making T as nearly as possible equal to 0° on the absolute scale, or in making S as large as possible.

The student should carefully note that in this illustration S and T are temperatures on the Centigrade scale measured from absolute zero; in § 188 we avoided defining the scale of temperature.

190. The Reversible Cycle.—The important feature of Carnot's cycle is that it is reversible. Instead of taking the order $A B C D$, it can be worked in the order $A D C B$.

First operation.—Let the condition of the working substance be represented by the point A . Pressure = p_1 , temperature = S , volume = v_1 .

Place the cylinder on the non-conducting stand, and let the substance expand; it will do so adiabatically, and the temperature will fall. When the temperature falls to T , the volume will be v_4 , and the pressure p_4 . These conditions will be represented on the diagram by D . Remove the cylinder to the cold body, whose temperature is T .

Second operation.—Let the substance still expand; it will do so at constant temperature, and the variations of temperature and pressure will be expressed by the isothermal $D C$. When the volume is v_3 and the pressure p_3 , stop the operation, and remove the cylinder to the non-conducting stand.

During this operation a quantity of heat has entered the working substance. It is equal to the quantity that flowed from it in the cycle (§ 188), when the volume was changed from v_2 to v_3 , that is, the quantity is h .

Third operation.—Press back the piston when the cylinder is on the stand. The variations of temperature and pressure will be expressed by the adiabatic curve $C B$. When the temperature is S and the volume v_2 and pressure p_2 , remove the cylinder to the hot body.

Fourth operation.—Continue to press back the cylinder. The temperature remains constant at S , and a quantity of heat, H , enters the hot body from the working substance. When the pressure is p_1 and the volume v_1 , stop the operation. The cycle is now complete, as the working substance is in exactly the same condition as at starting.

			Work done by the substance measured by	Work done on the substance measured by
First operation	$ADda$	
Second	„	...	$DCcd$	
Third	„	...		$CBbc$
Fourth	„	...		$BAab$

The nett work done on the substance is measured by the area $ABCD$.

To effect this work h units of heat have been taken from the colder body, and H units have been given to the hot body.

$$h - H = -ABCD = -W$$

or $H - h = W$

That is the same relation as in the direct action. We see that in this reversible engine a quantity of heat, H , at a given temperature, S , can enter the engine, and a quantity, h , can be given out at a lower temperature, T , with the result that useful work, W , is done; or a given quantity of heat, h , at a temperature, T , can enter the engine, and a quantity, H , can be given out at higher temperature, S , if work measured by W be done upon the engine.

191. A Reversible Engine the most Efficient.—Of all engines working between a temperature, S , and a lower temperature, T , and receiving a quantity of heat, H , at the higher temperature, the reversible engine is the most efficient.

The efficiency, we have seen, is $\frac{W}{H}$.

This proposition is proved by joining two engines. A is a reversible engine working between S and T , taking in heat H at S , giving out heat h at T , and doing useful work W . B is another engine working between the two temperatures S and

T, taking in heat H at S , and doing, *if possible*, more work, $W + w$.

Let a quantity of heat, H , from the hot body enter the engine B. As it is more efficient than the engine A, the work done is greater than W ; let us call the work done $W + w$. As it has transferred a greater quantity of heat into work, it will give up a less quantity to the cold body; call this amount $h - h'$. Let the work W be used to work the engine A in the reverse order. This work will take a quantity of heat, h , from the cold body, and give H units to the hot body.

The total result is that the hot body gives up and receives H units; that is, it does not lose heat.

The cold body receives $h - h'$ and gives up h units; that is, it loses h' units.

The useful work is $(W + w) - W = w$.

This can be repeated as often as we please, and thus the whole of the heat might be taken from a body by this combined engine without any further assistance, and changed into work.

This work is now available, and might be used in the reversible engine working in the reverse order, to raise the heat of a body at any temperature to a higher temperature, and thus ultimately all the heat of the universe might be changed to heat at a higher temperature.

Suppose a refrigerator were at 0°C ., and all surrounding objects at 100°C . If a reversible engine were not perfect, then it would be possible, by simply cooling the refrigerator below 0°C ., to do mechanical work; or it would be possible to raise a portion of the heat from 0° to heat at 100°C ., and allow this to flow back to heat at 0° , and in so doing produce mechanical work.

This is contrary to experience, and therefore we conclude that our hypothesis, namely, that any engine can have a greater efficiency between two given temperatures than a reversible engine, is false.

A reversible engine shows a maximum efficiency; that is, out of no other engine working between the same temperatures can more work be obtained for the same supply of heat, and

it follows that all reversible engines are equally efficient ; that is, the efficiency is independent of the working substance.

192. The Second Law of Thermo-dynamics.—From such reasoning the *Second Law of Thermo-dynamics* is deduced. The law is expressed in various forms—

“It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.”

“It is impossible by means of inanimate material agency to derive mechanical effects from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.”

193. Thomson's Scale of Temperatures.—Thomson has shown that Carnot's cycle leads to a method of defining temperature. In ordinary measurements we determine temperature from the expansion of mercury or other liquid inside glass, and, as has been seen, while two such thermometers agree at certain points, they do not agree at intermediate points, unless the same kind of glass and the same liquid be used.

The regularity in the expansion of air at constant pressure led to the selection of air or other gas as a thermometric substance. It is seen that for such gas—

$$v_t = v_0(1 + at)$$

If we wish to determine by calculation at what temperature the volume = 0 (we have no knowledge of such a temperature, and are not sure what changes would take place in a gas for some degrees above such a temperature,—certainly most of them would be liquefied (§ 123), perhaps solidified), we have—

$$\begin{aligned} v_t &= 0 = v_0(1 + at) \\ \therefore 1 + at &= 0 \\ t &= -\frac{1}{a} \end{aligned}$$

a is found by experiment to be 0.003665° on the Centigrade scale.

$$\therefore t = -\frac{1}{0.003665} = -272.85^\circ \text{ C. ; approximately, } -273^\circ \text{ C.}$$

This temperature is called the *absolute zero* of the Centigrade scale. The determination of the zero is dependent upon a particular substance—air, hydrogen, etc.

$$\text{Any temperature on this scale } T = t + \frac{1}{a}$$

The scale suggested by Thomson is independent of the working substance. In § 189 it is shown that if the working substance be a perfect gas, and temperature be measured from the absolute zero as deduced from the expansion of air, then the efficiency $= \frac{W}{H} = \frac{S - T}{S}$; that is, the efficiency is proportional to $\frac{S - T}{S}$, an expression in which temperature only is involved.

Carnot showed that this is true for any reversible engine if the difference of temperature be very small, so that the difference is a very small fraction of one degree. This can be extended to prove that generally the efficiency of a reversible engine depends on the temperature of the source and refrigerator alone, and is independent of the working substance.

Carnot's proof can be applied to ordinary Centigrade degrees as measured on an ordinary thermometer.

Thomson, assuming that—

$$\begin{aligned} \frac{W}{H} &= \frac{S - T}{S} \\ \text{or } \frac{H - h}{H} &= \frac{S - T}{S} \\ \text{or } \frac{H}{h} &= \frac{S}{T} \end{aligned}$$

is *rigorously* exact, and is from Carnot's cycle independent of the working substance, defined temperature thus—

The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the other respectively by a material system subjected to a complete cycle of perfectly reversible thermo-dynamic operations, and not allowed to part with or take in heat at any other temperature. Or—

The absolute values of two temperatures are to one another in the proportion of the heat taken in and the heat rejected in a perfect thermo-dynamic engine, working with a source and refrigerator at the higher and lower temperatures respectively.

$$\frac{S}{T} = \frac{H}{h}$$

S and T are temperatures as defined on Thomson's thermo-dynamic scale. H and h are measurable quantities.

The size of the degrees is a matter of convenience, as is also the zero of the scale. It is therefore admissible to attempt to adapt such a theoretic scale to our ordinary scales; for example, between melting point of ice and boiling point of water in the Centigrade scale there are 100 divisions; in the thermo-dynamic scale we can, similarly, make 100 divisions.

It is beyond the scope of this work to give all the steps in the calculation of the relation between the thermo-dynamic scale and the Centigrade scale.

The experimental work is that detailed in § 178. It was concluded by Thomson that—

$$\theta = t + \frac{1}{\alpha} - \frac{\kappa\tau}{\delta} \cdot \frac{1}{\log_{\epsilon} \frac{p}{p'}}$$

θ = temperature on thermo-dynamic scale.

t = „ „ Centigrade scale.

α = coefficient of expansion of the gas.

κ = specific heat of the gas at constant pressure in dynamical units.

τ = increase in temperature after the gas passes through the plug (§ 178).

δ = constant for gas = $\alpha p_0 v_0$.

p, p' = pressures on each side of the plug.

In the experiments τ was very small (see also § 178), and, save in the case of hydrogen, was negative. In all cases

$\frac{\kappa\tau}{\delta} \cdot \frac{1}{\log_{\epsilon} \frac{p}{p'}}$ was small; let it be indicated by γ , a small variable quantity.

Now, $t + \frac{1}{\alpha} =$ temperature measured from absolute zero of the Centigrade scale = T .

$$\therefore \theta = T \pm \gamma \text{ for all gases}$$

Thus the thermo-dynamic scale is obtained by adding or subtracting a small variable quantity to the Centigrade scale measured from absolute zero.

In one series of experiments the following results were obtained :—

Pressure of air forced into the plug (p) = 20.943 lbs. per sq. inch

„ atmosphere (p') = 14.777 „ „

Temperature of air before entering plug = 16° C.

Cooling effect (τ) = 0.105° C.

$$\kappa = 0.2375 \times 1390 = 330.125 \text{ foot-pounds}$$

$$\alpha = 0.003665$$

$$\therefore \frac{1}{\alpha} = 272.8$$

$$p_0 = 14.7 \times 144 = 2116.8 \text{ lbs. per square foot}$$

$$v_0 = \text{volume of 1 lb. of air at } 0^\circ \text{ C. and } 2116.8 \text{ lbs. per square foot pressure} = 12.39$$

$$\therefore \alpha p_0 v_0 = 0.003665 \times 2116.8 \times 12.39 = 96.122$$

$$\log_e \frac{p}{p'} = 2.3026 \log_{10} \frac{p}{p'}$$

$$\therefore \theta = t + \frac{1}{\alpha} - \frac{\kappa \tau}{\delta} \cdot \frac{1}{\log_e \frac{p}{p'}}$$

$$= 16 + 272.8 - \frac{330.125 \times (-0.105)}{96.12} \cdot \frac{0.4343}{\log 20.943 - \log 14.777}$$

$$= 288.8 + \frac{34.663}{96.12} \cdot \frac{0.4343}{0.15145}$$

$$= 288.8 + 1.03$$

$$= 289.83$$

The difference between the number of degrees on the Centigrade and thermo-dynamic scales, from freezing point to 16° C., will be very small. Therefore we conclude that

freezing point on the thermo-dynamic scale is approximately $273\cdot83^{\circ}$.

Careful calculations from many experiments showed that if the difference in temperature between melting point of ice and boiling point of water be represented by 100° , then the zero of the thermo-dynamic scale is $-273\cdot7^{\circ}$; if the difference in temperature be represented by 180° , the zero is $-460\cdot66^{\circ}$.

It is assumed that $p_0v_0 = p_{16}v_{16}$; this is not exactly true, and recognizing this difference would introduce a correction into the formula.

Thermo-dynamic scale.			Centigrade scale on air-thermometer (constant volume).
$273\cdot7 + 0^{\circ}$	0° (freezing point)
$+ 20^{\circ}$	$20 + 0\cdot0298^{\circ}$
$+ 40^{\circ}$	$40 + 0\cdot0403^{\circ}$
$+ 60^{\circ}$	$60 + 0\cdot0366^{\circ}$
$+ 80^{\circ}$	$80 + 0\cdot0223^{\circ}$
$+ 100^{\circ}$	$100 + 0^{\circ}$ (boiling point)
$+ 120^{\circ}$	$120 - 0\cdot0284^{\circ}$
$+ 200^{\circ}$	$200 - 0\cdot1798^{\circ}$

194. Freezing Point of Water lowered by Pressure.—This was first deduced by Professor James Thomson, from theoretical considerations.¹ The following are the essential steps: Let a mass of air be enclosed in a cylinder (the air-cylinder) similar to that described in § 188; let the air be compressed, and the temperature be 0° C.: the pressure on the piston we can call p . Let a small quantity of water be enclosed in an exactly similar cylinder (the water-cylinder), let the pressure be that of the atmosphere, and the temperature also 0° C. Place these cylinders together, with their bases in contact, the two forming an engine; heat will readily pass through the bases, but cannot escape from the engine as a whole, since the sides and pistons are perfect non-conductors.

Let the piston of the air-cylinder move, the compressed

¹ Transactions of the Royal Society of Edinburgh, 1849. Reprinted in Sir William Thomson's papers.

air doing work, until the pressure falls to 1 atmosphere. Heat will be needed ; this will flow from the water at 0° , and therefore part of it will freeze ; in freezing, water expands ; therefore, if the water-piston remain fixed, the pressure on the piston will become more than 1 atmosphere. The water is freezing under increased pressure, and we wish to determine its temperature while freezing. By allowing the water-piston to move, the water does work ; let it expand until the pressure falls to 1 atmosphere ; we have then water and ice at 0° C. Whatever the temperature may have been when freezing began, this will also be the final temperature of the air-cylinder.

Now press the air-cylinder back at 0° C. until the air attains its original volume, and consequently its original pressure ; the heat due to compression will flow through the bases, melt the ice, and the water-piston will be acted upon by the pressure of the atmosphere, which will do work on the piston. The heat of compression of the air will be that absorbed in expansion, and therefore the whole of the ice will again be melted ; the water will be at 0° C. ; the pressure is 1 atmosphere, and it will therefore occupy its original volume. Both air and water are in their original condition, and therefore any work done by the engine cannot come from the working substances.

The work done.—The distance traversed by each piston is the same in each operation. The water-piston, in doing work, begins at a pressure, as we have seen, greater than 1 atmosphere, and ends with a pressure of 1 atmosphere ; the mean pressure is therefore greater than 1 atmosphere. When work is done on it, the pressure throughout is 1 atmosphere ; therefore the water-piston, on the whole, does a certain positive amount of work. This can only come from the work done on the air-piston ; therefore more work must be done on the air-piston in compression than it does during expansion. This is only possible if the temperature during compression is greater than during expansion ; during compression it is throughout at 0° C., in expansion it is finally at 0° C., therefore when expansion began it must have been below 0° C. ;

but this was the temperature of the ice freezing under pressure, and hence we infer that, when ice freezes under pressure, its freezing point is lowered.

195. To Calculate the Lowering of the Freezing Point.—The last section shows that, in a mixture of ice and water, the pressure will remain constant as long as the temperature does not change—it will be the pressure corresponding to the given temperature; the isothermal for any degree will therefore be parallel to the line of volumes.

In a Carnot's cycle, let the working substance be a mass

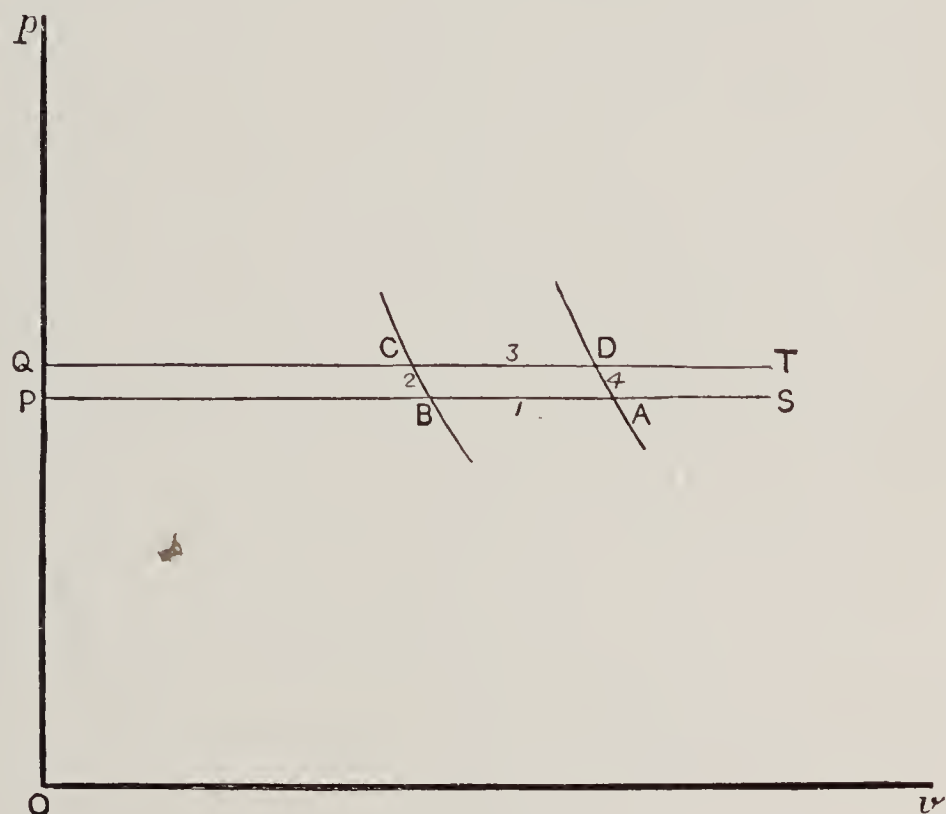


FIG. 134.

of ice which, if melted, will form rather more than 1 cubic foot of water, and let it be originally subjected to a pressure of 1 atmosphere; its temperature, therefore, will be 0° C. The temperature of the source S is 0° C., that of the refrigerator T is slightly below 0° C.

First operation.—Place the cylinder on the source, and let the piston do work on the ice, with the result that part of it melts. When 1 cubic foot of water is formed, stop the operation. The volume has decreased by 0.087 cubic foot, because

1 cubic foot of water at $0^{\circ}\text{C.} = 1.087$ cubic foot of ice at 0° . The first operation will be represented graphically by AB (Fig. 134). AB is the isothermal for the mixture at S° (*i.e.* 0°C.). $AB = 0.087$.

Second operation.—Place the cylinder on the non-conducting stand, and force the piston down; the temperature will fall and the pressure will increase; the adiabatic curve BC will be described. When the temperature is $-t^{\circ}\text{C.}$, the temperature of the refrigerator, stop the operation.

Third operation.—Remove the cylinder to the refrigerator T , and let the working substance do work on the piston; the volume will increase, but the pressure and temperature will remain constant, and the isothermal CD for T (*i.e.* $-t^{\circ}\text{C.}$) will be described. Stop the operation when the volume is such that it is represented by D , that is, when the isothermal crosses the adiabatic curve passing through A .

Fourth operation.—After placing the cylinder on the stand, let it further expand; it will do so adiabatically. When the temperature is that of the source S , the pressure will be 1 atmosphere, and the temperature will be 0°C. The working substance is now, in all respects, in exactly the condition in which it started, and the whole process is reversible.

The work done is represented by the area $ABCD$; the isothermals are very near to each other; and the area, neglecting very small differences, will be the rectangle whose base is BA , and vertical height PQ .

$$\therefore \text{work done} = BA \times PQ$$

$BA = 0.087$ foot; $PQ = p =$ difference in pressure in pounds per square foot.

$$\therefore \text{work done} = 0.087p \text{ foot-pounds}$$

But in a cycle—

$$\frac{\text{Work done}}{\text{Heat absorbed}} = \frac{\text{difference of temperature between } S \text{ and } T}{\text{temperature of source}}$$

temperature being on the absolute scale.

To melt 1 cubic foot of ice, $80 \times 62.5 = 5000$ thermal units are needed.

$$S - T = t^{\circ} \text{C.}; \quad S = 273.7$$

$$\therefore \text{work done in dynamical units} = 5000 \times 1390 \times \frac{t}{273.7} \text{ ft.-lbs.}$$

$$\therefore t = \frac{0.087 \times 273.7}{5000 \times 1390} p = 0.00000343 p$$

If we express p in atmospheres (P), we have the pressure of 1 atmosphere = 144×14.7 lbs. per square foot = 2116.8.

$$\begin{aligned} \therefore t &= 0.00000343 \times 2116.8 P \\ &= 0.0073 P \end{aligned}$$

If the pressure be increased by 1 atmosphere, the temperature of freezing will be lowered by about 0.0073°C. ; and if the pressure be increased to about 137 atmospheres, the temperature will be lowered 1°C.

By similar reasoning, it can be shown that the freezing points of wax, lead, silver, and substances generally that expand in liquefaction, are raised by increased pressure.

196. Adiabatic Curves.—Entropy.—Reference was made in § 184 to the fact that, as in isothermal curves the temperature was constant, so in adiabatic curves there was a constant quantity. The condition of adiabatic expansion or contraction is that no heat shall enter or leave the working substance; of course, seeing that during adiabatic change, work is done by or on the working substance, there will be a loss or gain of heat-energy due to transformation of energy. We have seen that, in Carnot's engine, working between two temperatures, S° and T° (measured on the thermo-dynamic scale), if H_1 and H_2 be the heat taken in and given out respectively at the two temperatures—

$$\frac{H_1}{S} = \frac{H_2}{T}$$

H_1 is the heat taken from the source at temperature S° (the isothermal is A B, Fig. 133); H_2 is the heat given to the refrigerator at temperature T° (the isothermal is C D).

Between A B, C D we may have any number of isothermals crossing B C in points E, F, G, H, etc. (the student can insert

these lines). In passing from the adiabatic B C to the adiabatic A D, along the isothermal through E, F, G, . . . there will be an amount of heat, H_2' , given out at temperature T_2° .

By the above equation—

$$\frac{H_1}{S} = \frac{H_2}{T} = \frac{H_2'}{T_2}$$

Therefore, in passing from any adiabatic curve, A D, along an isothermal, to another adiabatic curve, B C, the ratio of heat taken in or given out, to the temperature at which it is taken in or given out, is constant.

For this reason a quantity of the form $\frac{H}{T}$ is regarded as a characteristic quantity of a body. If $\frac{H}{T}$ remains constant, the body is changing adiabatically, or along an adiabatic curve $\phi = \frac{H}{T}$ is a constant.

This quantity ϕ is called the entropy.

$$\phi = \frac{H}{T}$$

We are generally dealing with differences of entropy, and therefore the absolute zero of entropy, which would be its condition when deprived of all heat, need not be known; it is sufficient to select any arbitrary zero.

Clerk Maxwell reckons the entropy from a standard state defined by a standard temperature and pressure.

“The entropy of a body in any other condition is then measured thus: Let the body expand (or contract) without communication of heat till it reaches the standard temperature, the value of which, on the thermo-dynamic scale, is T . Then let the body be kept at the standard temperature, and brought to the standard pressure, and let H be the number of units of heat given out during this process. Then the entropy of the body in its original state is $\frac{H}{T}$.”

Let $\phi_1 = \frac{H_1}{T_1}$ = entropy of a body A at T_1°

„ $\phi_2 = \frac{H_2}{T_2}$ = „ „ „ B „ T_2°

Let heat pass from the body at the higher temperature, T_1° , to the body at the lower temperature, T_2° ; let h be the quantity of heat that passes.

The entropy of A is now $\phi_1' = \frac{H_1 - h}{T_1}$

„ „ B „ $\phi_2' = \frac{H_2 + h}{T_2}$

$$\begin{aligned} \therefore \text{the gain of entropy} &= (\phi_1' + \phi_2') - (\phi_1 + \phi_2) = \frac{h}{T_2} - \frac{h}{T_1} \\ &= h \left(\frac{T_1 - T_2}{T_1 T_2} \right) \end{aligned}$$

This is necessarily positive, as T_1 is greater than T_2 .

Considering a series of such changes among a system of bodies A, B, C, D, . . . we see that there will always be a gain in entropy; that is, the entropy of a system always tends to a maximum; and, generally, the entropy of the universe tends to a maximum.

Referring to Carnot's cycle, the isothermals can be represented by t_1 and t_2 , and the adiabatics by ϕ_1 and ϕ_2 . Passing from ϕ_1 to ϕ_2 along t_1 , the heat taken in is $t_1(\phi_2 - \phi_1)$. Passing from ϕ_2 to ϕ_1 along t_2 , the heat given out is $t_2(\phi_2 - \phi_1)$.

\therefore the work done equals the difference $= (t_1 - t_2)(\phi_2 - \phi_1) =$
area ABCD

EXAMPLES. XII.

1. Write out the first law of thermo-dynamics, and state how it was deduced.

2. Point out the defect in Mayer's method of determining the mechanical equivalent of heat.

3. Compare the methods of Joule, and Joule and Thomson, in testing Mayer's hypothesis. What are the advantages of the latter method?

4. How can the ratio of the two specific heats be determined from

the velocity of sound in air? Explain Laplace's correction of Newton's formulæ.

5. What are the essential points about isothermal and adiabatic lines?

6. Explain and illustrate "a cycle of operations."

7. Why is there the need for the limitations in the third of Carnot's operations?

8. Prove that a reversible engine is, of all engines, the most efficient.

9. How did Sir William Thomson determine his thermo-dynamic scale? In what respects does it differ from the Centigrade scale (*a*) of an air-thermometer, (*b*) of a mercurial thermometer?

10. What do you mean by the efficiency of a steam-engine? What is the theoretical efficiency of a steam-engine whose boiler is at 150°C. , and whose condenser is at 40°C. ?

11. A definite volume of steam, on entering the cylinder of a steam-engine, possesses a definite amount of heat, which is in part communicated to the cylinder, and in part carried away by the steam after it has done its work in the cylinder. Supposing all the heat thus communicated and carried away to be collected, would it or would it not be equal to the heat possessed by the steam immediately before entering the cylinder? If there be a difference, what is the cause?

12. Show from Carnot's cycle that the temperature of fusion of wax will be raised by pressure.

13. A certain heat-engine is supposed to be perfect: if the temperature of the source is 280°C. , and that of the refrigerator is 120°C. , find the efficiency. If 250 heat units are supplied by the boiler, find the work done in foot-pounds.

14. A 1500-lb. shot strikes a target with a velocity of 1000 feet per second: if all the kinetic energy be transformed into heat, and all the heat generated be utilized in heating 1000 lbs. of water at 0°C. , find the final temperature.

CHAPTER XIII.

APPLICATIONS—CLIMATE.

197. General.—In the preceding chapters reference has been made to many applications of the theory of heat to climate, ocean and air circulation, heating by hot water, etc.; a complete explanation, however, was impossible until the general theory of heat was understood.

198. Heating of Buildings.—Open Fireplaces.—Heat, the result of the combustion of coal, is radiated, and warms the room. Combustion is made possible by the fresh air passing over the burning coals and bringing the necessary supply of oxygen. The air in the chimney is heated; it becomes less dense than a similar column of colder air at the temperature of the room, and circulation ensues.

The velocity of the draught depends upon the height, and therefore the chimney should be high enough to produce sufficient draught for any required purpose. The chimney should not be wider than necessary, otherwise there is a tendency for descending currents to form. The air entering the chimney should, for the best combustion, pass over the fire; this is attained by making the entrance to the chimney small, and just above the fire. The effect of the sheet of iron that is sometimes placed in front of the fire is to make all the air pass through the fire; the combustion is thereby improved. Bright metal or tiled plates serve to reflect the heat, while the fire-brick back becomes hot and acts as a radiator. The pleasant feelings associated with a bright fire, and the effective aid such a fire is to ventilation, makes the open fire popular; it is, however,

far from economical, and probably not more than 10 per cent. of the heat of combustion is utilized.

Gas fires in some cases take the place of open fires. The heat is more under control, and, as the stove generally projects into the room, the metal body and the pipe leading to the chimney become hot, and serve as radiators. The heated gases become well cooled before entering the chimney, and the economy is therefore greater. Gas fires frequently produce an unpleasant, irritating feeling, on account of the temperature of the air of the room becoming so high that it becomes very "dry." This can be remedied by keeping vessels filled with water in the room, so as to keep the air nearer its point of saturation. In comparing the relative efficiency of gas and coal, it must be remembered that gas is a more expensive form of obtaining heat.

199. Hot-Water Apparatus.—The boiler is placed as low in the building as possible, and should be lower than any of the pipes. The feed-pipe should enter the bottom of the boiler, and the pipe that conducts the hot water should leave at the highest point; this outflow pipe should be, as far as is practicable, vertical. The heated water ascends (§ 138) the vertical pipe, the column being less dense than the column in the return-pipe. During its return the water passes through suitable iron coils, heats these coils, and, by radiation, heat is communicated to the various apartments. A cubic foot of water weighs about $62\frac{1}{2}$ lbs.; therefore, in cooling one degree, $62\frac{1}{2}$ thermal units will be liberated. One cubic foot of air weighs 0.0807 lb., and its specific heat is 0.2375, therefore $0.0807 \times 0.2375 = 0.0192$ thermal unit is needed to heat 1 cubic foot of air through one degree, and therefore 1 cubic foot of water cooling one degree will, theoretically, heat $62.5 \div 0.0192 = 3250$ cubic feet of air through one degree. Knowing, then, the supply of air that must be heated, we can determine the size of pipes required, and the amount of water that must pass through per minute at a given temperature, to properly heat any room. Rooms should be kept at from 54° to 68° F. during the day. The useful heat obtained will depend upon the temperature of the fire, the surface of

the pipe, and also, as questions of conductivity and radiation will be involved, upon the nature of the pipe. As the radiator, iron (or, better, copper) will be a suitable material; the pipes joining the radiators should be covered by some non-conducting substance, such as felt, if such pipes are not required for heating purposes.

200. Heating by Steam.—In heating with hot water, the high specific heat of water is a great advantage, seeing that the water cools slowly. The system is of great advantage for a steady supply of heat at a temperature below 100° C. The efficiency of a radiator is greatly increased by raising the temperature. This can be attained by using steam; by heating the steam under pressure (§ 117) the temperature can be raised above 100° C., and the radiators can be kept at any desired temperature by increasing the pressure. Smaller pipes can be used for connecting the radiators, and thus less heat will be lost by radiation from the connecting pipes. If the pressure of steam ceases, then the amount of water condensed is, compared with the amount that would be present in hot-water pipes, small, and therefore the temperature will rapidly fall, despite the heat liberated in condensation, unless the fires be attended to. This is in many cases an advantage, because, as soon as no further heat is required, there ceases to be a waste of energy.

201. The Heat of the Sun.—The principal source of heat, as we have seen in chapter xi., is the sun. The radiant energy passes through dry air almost undiminished in quantity. Water vapour and the dust-particles absorb certain light-rays, and give rise to rain-bands in the visible spectrum; they also have an absorptive effect upon the heat-rays. The radiant energy at the surface of the earth is changed into sensible heat, and warms the surface, and the heat is again radiated into space. It is now, however, proceeding from a source at a comparatively low temperature, and the water vapour has a greater absorptive effect upon such radiation; therefore the earth will lose less heat when surrounded by air containing vapour than when surrounded by comparatively dry air. Probably a greater effect is due to the condensed water-particles and the dust-

particles that have been shown to be always present in the air. Clouds serve also as reflectors, and again prevent loss of heat into stellar space.

202. Dust.—The action of dust in climatology has been investigated by Mr. John Aitken, who has shown that dust-particles can always be detected in the atmosphere. They are due to the meteorites that reach the atmosphere—cosmic dust—and to the dust carried into the atmosphere by winds, or projected into it by volcanoes. Dust-particles are most frequent over towns, and decrease as we reach pure mountain air. The result of Mr. Aitken's experiments is to show that water vapour cannot condense unless dust-particles be present, and that therefore condensation is impossible in an atmosphere freed from dust. The presence of the dust, as a nucleus on which the water can condense, is thus an essential condition.

203. Water Vapour.—The presence of water vapour has already been discussed in the chapter on hygrometry. Remembering that water vapour is five-eighths the density of dry air under similar conditions, and that any mixture of water vapour and air is less dense than dry air, we see that the heating of the surface of the earth, which by conduction heats the lower strata of air, combined with the result of the water vapour entering the air on account of evaporation, will be to make the stratum of air nearest the ground less dense than that above, and therefore there will be an ascending current of atmospheric air.

204. Pressure and Temperature, and Altitude.—The atmospheric pressure is due to the column of air above us, and it follows that, generally, as we ascend the pressure will be reduced. As the greatest action of the sun's heat is to raise the temperature of the surface of the earth, the lower strata become the most heated, and generally the nearer the earth, the higher the temperature. The heated air, as it ascends, passes into a region of lower temperature, and therefore expands. In so doing it does work, and there will be a consequent fall of temperature. If the air were perfectly dry, it has been computed that the fall would be 1° F. for every 180 feet. There are, however, many factors to consider.

The air contains moisture that, with the fall of temperature, condenses. In condensing, heat is liberated, and the fall in temperature is retarded. The rate of fall of temperature will vary with the conditions, but an approximate rate is a fall of 1° F. for every 300 feet.

205. Condensation of Water Vapour.—If the atmospheric air be cooled sufficiently, there will be condensation of the moisture. The cooling may be produced—

(1) As we have seen above, by the ascent of moisture-laden air into the higher altitudes.

(2) Warm and damp currents may be cooled by coming in contact with cold masses of mountains, or, in certain cases, of earth.

(3) Warm and damp currents may meet colder currents.

In all cases dust-particles must be present.

Condensation and the production of rain due to the first cause is most strikingly seen in the tropics. The rapid evaporation of water and the heating of the air produce a powerful up-current; this is due to the work done in expansion and also to the fall in temperature due to the altitude. The air is cooled, and part of the moisture condenses,—the result is almost continuous rain in the tropical regions known as the zone of constant precipitation; in the condensation, however, heat is liberated, and excessive condensation is retarded.

To the second cause is due the condensation of vapour as rain on our west coasts, and in certain cases to the ground fogs near cold and clayey soils. The west winds bring air laden with moisture; these winds impinge upon the mountains on the west coast, and the stratum at the base is in part cooled, and rain falls; but the air is forced to ascend, therefore the first method comes into play, and this, added to the coldness of the higher parts of the ranges, produces the heavy rainfall.

The third mixture is not so effective as was at one time supposed. The following calculation is given in a well-known text-book.

“Suppose a cubic metre of air at 10° C. mixes with a cubic metre of air at 20° C., and that they are respectively saturated with aqueous vapour. It is easily calculated that

the weight of water contained in the cubic metre of air at 10°C . is 9.397 grams, and in that at 20°C . is 17.153 grams, or 26.559 grams in all. When mixed they produce 2 cubic metres of air at 15°C .; but as the weight of water required to saturate this is only $2 \times 12.8 = 25.6$ grams, the excess, 0.95 gram, will be deposited in the form of mist or cloud."

But 0.95 gram, condensing, liberates 0.95×536 thermal units = 509 thermal units; 2 cubic metres of moist air at 15°C . weigh about 2440 grams, and taking the specific heat as 0.2375 (dry air), we see that the temperature cannot fall to 15° .

Calculation has shown that the rainfall from this source must be small.

206. Dew.—Dew is the condensed vapour formed on terrestrial objects; the vapour is condensed on the object without passing through the form of cloud and then falling as rain. The explanation of this phenomenon is due to Dr. Wells.

After sunset, if the sky be clear, heat is radiated from the earth, and the temperature falls; in the absence of much water vapour and cloud, the temperature of parts of the earth falls below the dew-point for the lowest stratum of air, and dew is deposited on these objects.

A cloudy night, the presence of much aqueous vapour, prevents the radiation, and dew is not formed; it is also prevented by wind. We have seen that rough bodies radiate heat most rapidly; dew is hence formed on grass and twigs when none is formed on bright objects—gravel or bright metal tools. The formation on gravel and metals is further prevented by the fact that they are good conductors of heat, and the loss due to radiation is made up by conduction.

The slightest covering of matting or similar substance over plants is sufficient to prevent the falling of temperature due to radiation to a point that would kill the plants.

If the temperature be below freezing point, the dew is at once frozen, and appears as *hoar-frost*; if the dew freezes after it is deposited, the result is *black frost*.

Investigations of Mr. Aitken show that the excessive dew formed on some plants is not due to the condensation of

vapour of the air alone, but is also due to vapour given out by the plant.

207. Clouds and Rain.—When moist air rises to high altitudes, condensation takes place when the temperature of the dew-point is reached; the small particles of condensed water form clouds. The transparency of the water vapour is replaced by a certain opacity of these numerous droplets, and owing to the number of the reflecting surfaces, they become visible. These droplets are always falling to the earth, and in falling small ones coalesce into larger ones; if they pass through an unsaturated stratum, they may again evaporate. Rain is therefore always descending from the base of a cloud, but it may not in all cases reach the earth. If evaporation does not take place with sufficient rapidity, the drops reach the earth as rain. In condensation heat is liberated, explaining the rise in temperature that accompanies many of our rains. A gallon of rain, for example, in condensing, will liberate 5360 units of heat; as the specific heat of air is low (0·2375), it is at once evident that the liberated heat will have a marked effect upon the temperature.

208. Snow and Hail.—If condensation takes place below freezing point, the water crystallizes as ice, the general form being hexagonal; a variety of shapes are formed, and these crystals join and form snowflakes. Snow sometimes falls when the temperature is a few degrees above freezing point, but the limit is soon reached.

The formation of hail has not been satisfactorily explained.

209. Mist and Fog.—The name *mist* is applied to the “cloud” formed near the surface of the earth by the cooling of the moist air below the dew-point; it differs from *fog* in that the particles of water are larger, and it more readily wets objects than fog.

The fogs in large towns are formed by the vapour condensing on the small particles of smoke; the soot-particles, covered with water vapour, remain suspended in the atmosphere, and form the black fogs.

Warm air may be cooled by cold currents of water or a cold object, and a fog is produced; this explains the dense

fogs formed near icebergs. The dense fogs near Newfoundland are due to the cold Arctic current meeting air warmed by the Gulf Stream (§ 215).

In winter, running streams (above 32° F.) are frequently warmer than the stratum of air above them; evaporation takes place, and the air becomes more than saturated for its temperature, and a fog is formed.

On clear nights, on account of rapid radiation, the temperature of the ground falls; the stratum of air nearest the ground is cooled below its dew-point, and dew is deposited. This stratum is now saturated, and colder than those above it; if the configuration of the ground be such as in river valleys or on low-lying fields, the colder air above flows down to the low-lying parts, and by mixture produces a fog. These fogs are thin layers, and disappear with the morning sun, the temperature soon rising sufficiently high to enable the air to contain the excess of water vapour that constituted the fog.

210. Wind.—If we imagine the atmosphere to be formed of concentric layers around the earth, the lowest layers will be the most dense, and, as we ascend, the density of the layers will diminish. If from any cause the lowest layer be heated (this is done in nature by the heated earth), that layer will expand and lift the layers above,—a blister, so to speak, will be formed, and the air will flow away on all sides in the higher regions of the atmosphere. This reduces the mass of air over the particular spot, and consequently there will be a reduction of pressure as measured by the barometer.

At the surface of the earth the heated spot will become a centre of low pressure compared with surrounding places, and, following the law of fluids, air will flow from the surrounding places to this spot. In the highest layers there will be a current away from the spot, and thus a general circulation will ensue; this is assisted from the fact that with heat evaporation takes place, and the mixture of heated air and water vapour formed is relatively less dense than the air immediately above it, and thus the heated moist air will rise.

211. Land and Sea Breezes.—Land absorbs radiant heat from the sun more readily than the sea; its specific heat

is also lower than that of water; the water also reflects the radiant energy more readily than land, and its incessant motion presents fresh layers to be heated, and this again prevents any great increase in its temperature.

During the day, then, the land will become relatively warmer than the sea, the raising of the layers will take place over the land, and the air in the upper layers will flow seaward; a reduction of pressure follows over the land, and a current of air (the sea breeze) sets in from the sea. As soon as the sun sets, radiation takes place rapidly from the land; the temperature falls, and soon falls below that of the sea, which tends, for the reasons given above, to keep fairly constant. It follows that the low pressure will now be over the sea, and a land breeze sets in.

212. Effect of the Earth's Rotation on Winds.—

The direction a wind or current takes with respect to the earth will be modified by the motion of the earth beneath it. Suppose a mass of air in the northern hemisphere, at rest compared with the earth, starts with a velocity of say 20 feet per second; at the end of 1 second let it reach a point that is moving eastward with a velocity of 2 feet per second greater than the velocity of the starting-point. Then, if we consider a small portion of the earth's surface—for all purposes a plane—and neglect any effect of friction between the air and the earth, this current will appear, to a person in the second position, to be moving from the north-east; that is, if the wind be indicated on a map, the effect of rotation has been to turn the wind to the right hand. This effect will be seen under the above conditions in whatever direction the current moves in the northern hemisphere; in the southern hemisphere the effect will be to twist it to the left hand. But in the general conditions of atmospheric circulation we have a mass of land and water surrounded by a mass of air; under such conditions, if we neglect any effect of friction, a particle of air moving towards the equator would have a velocity eastward, compared with that of the earth, that would vary inversely as the distance from the axis of rotation. This would, in the northern hemisphere, again change a wind that originally was due south into

one that is from the north-east ; a due north wind would be changed into one that was from the south-west ; and the change can be readily applied to the southern hemisphere.

In reality, the lamina of air above the earth drags upon the surface and also against the lamina above it, so that a wind starting from the calms of Cancer would, as it journeyed towards the equator, be receiving an impetus from the rotating mass of the earth that would tend to make its motion less from the east than the above considerations would suggest ; and the wind would tend to have the same absolute velocity as the sea and land beneath it.

213. Atmospheric Circulation.—Recorded observations show that a belt approximately near the equator is a region of low pressure, that a belt in each hemisphere between 20° and 30° latitude is a region of high pressure, and that the poles are regions of low pressure ; there will then be on the surface of the earth a wind from this “border belt” in each hemisphere, equator-wards and pole-wards, and by § 212 the winds to the equator will be easterly winds, known as the trade winds ; the winds to the pole will be westerly, and form the north-westerly and south-westerly winds in the north and south hemispheres respectively.

These surface winds necessitate other currents in the upper regions of the atmosphere in (generally speaking) opposite directions to the surface winds.

The following explanation of atmospheric circulation was first fully described by the late Professor James Thomson, in 1857. He based his explanation on a general theory published, in 1735, by Hadley. The whole question is discussed in the Bakerian Lecture for 1892, by Professor Thomson.¹

The rising of the heated air near the tropics produces a lowering of pressure and a current, which, for the present, we can imagine starting from the calms of Cancer (the description that follows refers to the northern hemisphere ; the student can readily adapt the explanation to the southern hemisphere) ensues. This wind, by the last section, will blow, not due south, but from the north-east ; the excess of westerly direc-

¹ “Philosophical Transactions,” 1892.

tion over the earth will, however, by friction of the earth, be diminished, so that as it approaches the equator it becomes less and less an easterly wind, and it ascends with an absolute easterly velocity but slightly less than the rotational velocity of the earth; that is, its absolute easterly direction is approximately 1000 miles an hour, while its relative westerly direction compared with the earth is approaching zero. We can with convenience adopt the convention of Professor Thomson,

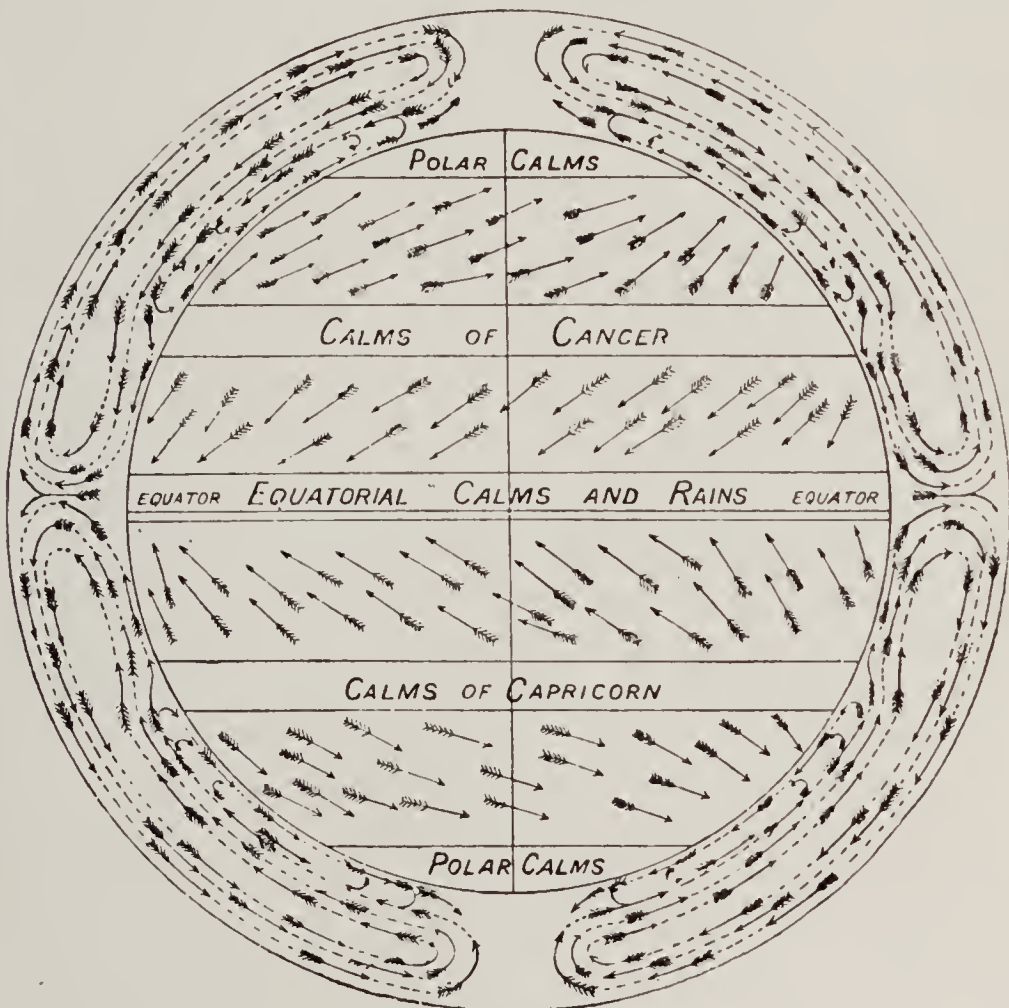


FIG. 135.

and call air that has no eastward or westward motion relative to the earth's surface as having *par*, or being *at par* of revolutionary velocity, and likewise, to use the designation *over par* of revolutionary velocity to signify eastward relative motion, and *under par* to signify westward relative motion.

The air, then, rises at the belt near the equator with *par* revolutionary velocity, and in the upper regions flows north and

south. If we follow the northern current, we see that, as it advances to the north, it has a greater eastward velocity than the earth beneath it; it cannot lose its revolutionary momentum by reason of any fluid above it, and will be but slightly affected by the current beneath it; that is, it is moving north with over-par revolutionary velocity. It gradually cools as it moves towards the higher latitudes, it is also deprived of part of its water vapour, and becomes more dense; this north-moving sheet of air engirdling the earth will descend in the middle and higher latitudes, and should then return towards the equator. Remembering that its revolutionary velocity is over par, it should return as a wind from the *north-west*. As a result of observation, the general wind in middle latitudes is from the *south-east*. To explain this, Professor Thomson states that the greatest amount of air does return as a current from the *north-west*, and that this constitutes the main return current. This return current, when it turns south, is at over-par revolutionary velocity, and there will be a sheet of air engirdling the earth beneath the upper current (also at over par), and this sheet of air at over-par revolutionary velocity induces, upon a comparatively thin lamina of air next to the earth, a wind towards the north-east, that is, pole-wards, with over-par revolutionary velocity (Fig. 135, after Thomson).

He illustrates this by the following experiment:—

“If a shallow circular vessel with flat bottom be filled to a moderate depth with water, and if a few small objects, very little heavier than water, and suitable for indicating to the eye the motions of the water in the bottom, be put in, and if the water be set to revolve by being stirred round, then, on the process of stirring being terminated, and the water being left to itself, the small particles in the bottom will be seen to collect in the centre. They are evidently carried there by a current determined towards the centre along the bottom in consequence of the centrifugal force of the lowest stratum of the water being diminished in reference to the strata above, through a diminution of velocity of rotation in the lower stratum by friction on the bottom. The particles, being heavier than the water, must in respect of their density have

more centrifugal force than the water immediately in contact with them, and must therefore, in this respect, have a tendency to fly outwards from the centre; but the flow of water towards the centre overcomes this tendency, and carries them inwards, and thus is the flow of water towards the centre in the stratum in contact with the bottom palpably manifested."

The indraught to the centre of the vessel is similarly observable when the vessel itself is rotating, provided that its velocity of rotation is less than that of the fluid.

Applying this to atmospheric circulation, we have in middle latitudes and towards the poles an upper current from the equator to the poles with *over-par* revolutionary velocity, below this the main return current to the equator also with *over-par* velocity, and the lamina in contact with the earth still with *over-par* velocity, but with an indraught towards the poles; it is this lowest stratum that is observed, and forms the general south-west winds of the middle and northern latitudes of the northern hemisphere.

There will be, then, three strata (see Fig. 135) of air in the higher latitudes. If we follow the middle main return current above the lowest strata, we shall expect that it will gradually lose part of its *over-par* velocity, seeing that it has to drag forward the lower layer; about the calms of Cancer it has lost so much of its *over-par* revolutionary velocity that it is no longer able to have an effective result on the lowest lamina, and therefore the indraught northward ceases. The return current now forms the lowest stratum, and comes under the influence of the indraught towards the equator, and the circulation is complete, the north-east trade wind again being produced.

The lamina below the return main current as it flows north is gradually deprived of its *over-par* velocity, with the result that over the pole there will be impounded a great mass of air; that, it is suggested, lies there, and is only brought into circulation by being dragged away by the great upper current that is possessed of great revolutionary motion. It will be seen that the mid return current is also the return current for the lowest lamina.

The general direction will be modified and altered by the land and changes in climatic conditions. For the particular discussion, as well as reference to particular winds, the student may consult the work in this series dealing with Physiography.

214. Water Circulation.—Ocean Currents.—The result of deep-sea soundings has shown that the ocean, save a comparatively thin upper stratum (that varies in depth with position and time of the year) is composed of water but slightly above freezing point. This mass of cold water is probably due to the action of the ice and cold of the polar regions.

In the equatorial regions the sun heats the surface of the sea; expansion takes place, and a circulation ensues that would be primarily a surface current from equator to pole, and a current at the bottom of the ocean from pole to equator. The currents are modified by the rotation of the earth (compare pp. 321, 322) and the direction of the winds.

215. The Gulf Stream.—As a result of the trade winds and the rotation of the earth, a current sweeps across the South Atlantic; this current is divided into two portions by Cape St. Roque, the northern portion flowing along the coast of South America into the Caribbean Sea, and is reinforced at the islands by a current from Cape Verde Islands.

The large mass of warm water from tropical regions crowded into the Caribbean Sea is forced through the Straits of Florida, and is reinforced by other branches of the current, that, divided by the islands from that which entered the Caribbean Sea, has swept past Cuba and St. Domingo, and joins the current generally called the Gulf Stream. The stream passing through the straits is 40 miles wide, 3000 feet deep, and has a velocity at the middle of about 5 miles an hour. Sweeping north, it grows wider and shallower; near Newfoundland its width is 320 miles, in the middle Atlantic 800 miles. The prevailing south-west winds now influence it. In mid-Atlantic it divides; one branch, either a continuation of the Gulf Stream, or due to the action of the prevailing winds, a new current formed out of the water brought by the Gulf Stream, flows to the British Isles, Iceland, and Norway; the other, affected by the earth's rotation, turns to the right, and

passes round by Spain and the north coast of Africa, and joins the main equatorial Atlantic current; the main currents surround a central mass of water forming the Sargasso Sea.

It should be noticed that a marked effect of the Gulf Stream on these isles, as regards heat, is due, not directly to the current of water, but to the fact that the prevailing south-west winds flow over it, become charged with moisture, and, on condensation taking place, heat is liberated (§ 207).

216. Electric Pyrometer.—In § 152 it was seen that if one junction of two metals be kept at a higher temperature than the other junctions, a current is produced that varies with the difference in temperature of the junctions. Instruments have been made based on this principle for the measurement of high temperatures.

Two wires—for temperatures up to about 225° C., copper and iron may be used—are joined at one junction by wrapping platinum wire round them for a short distance,—they are otherwise kept separate throughout their lengths. The wires are placed in a porcelain tube; the other ends are soldered or joined to thick copper wires that lead to a galvanometer. The soldered or joined ends are kept at a constant temperature by immersing them in water at the temperature of the room, or by placing them in melting ice.

The ends joined by platinum are now subjected to known temperatures by immersing them in solutions or in metals at their boiling points, and the deflection of the galvanometer is observed for each of these known temperatures. The deflection is kept small by introducing suitable resistances into the circuit; from the observed deflections estimates are made as to the temperature indicated by any difference between the observed deflections.

By placing the ends of the wires in any enclosure, it is thus possible to estimate the temperature.

At 276° C. in the case of iron and copper the neutral point is reached, and, if the temperature be raised higher, the current is reversed; before this temperature is reached the deflections produced are small for a slight change of temperature.

In Becquerel's pyrometer, platinum and palladium wires are used; these are less fusible than copper and iron, and, proceeding as above, a scale can be formed for these wires.

217. Siemens's Electrical Pyrometer.—The current from a battery, B, flows along the wire B A C; at C it divides. One portion passes along the coiled platinum wire D to E, and enters one coil of the differential galvanometer G by *a*, leaves it by *b*, and, passing along the wire H B, returns to the battery B. The other portion of the current flows from C along the wire C J to the resistance box R; it passes through the resistance box, and then flows through the other coil of

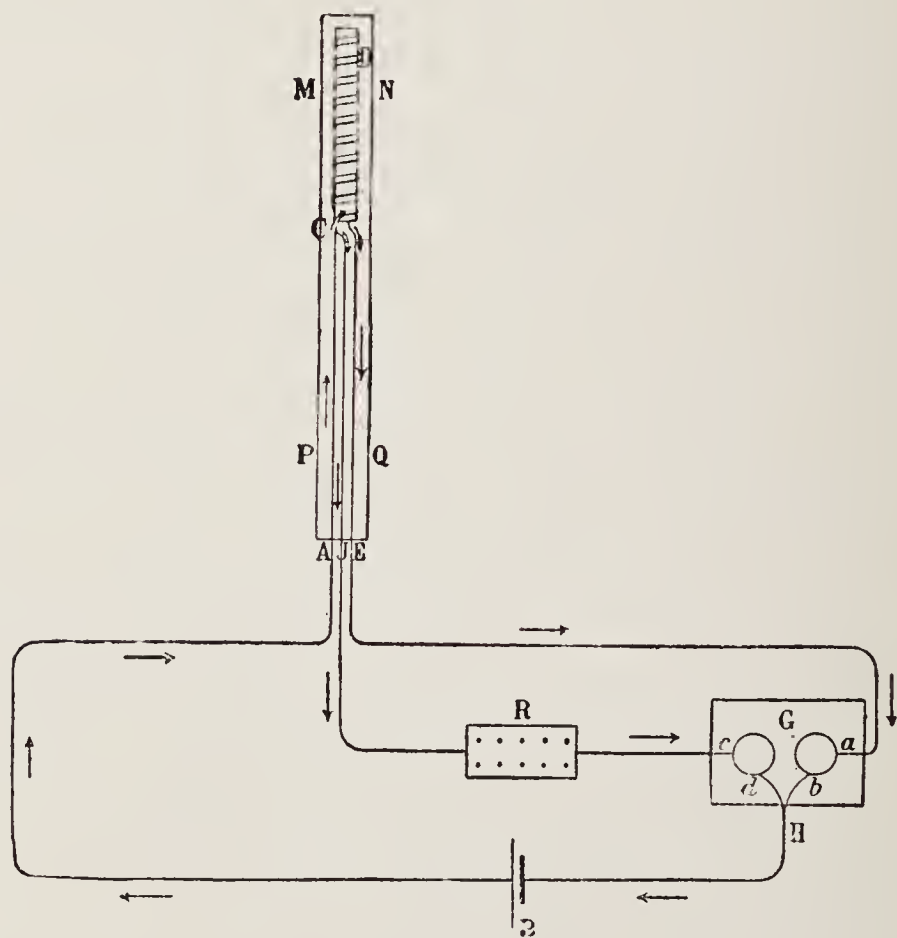


FIG. 136.

the differential galvanometer G; it enters this coil at *c*, and leaves it at *d*; it then flows to H, and passes along H B to the battery.

If the resistance of the branch C D E *a b* H be equal to the resistance of the branch C J R *c d* H, the current will divide

into equal portions at C, and there will be no deflection of the needle of the galvanometer.

C D is a coil of platinum wire wrapped round a fire-clay cylindrical cell; the wire is surrounded by asbestos, that is kept in position by platinum foil; the protected coil is placed inside a long wrought-iron tube, M N, and is kept in position by a packing of lime; the packing of lime also serves to keep the wires C A, C J, and D E in position.

In graduating the instrument, the end of the tube containing C D is placed in baths whose temperatures are known,—for example, boiling water, boiling zinc; the resistance of C D is increased, and the resistance of R is adjusted so that there is no deflection in the galvanometer. The results are plotted so that the resistances in ohms form the ordinates, and the temperatures the abscissæ; it is found that practically the curve formed is a straight line.

In order to determine any unknown temperature, the closed end of the tube is subjected to the unknown temperature, and the resistance necessary to prevent any displacement of the galvanometer needle is read. From the plotted curve the unknown temperature is readily deduced.

By means of pyrometers of this description it is possible to determine temperatures up to 1200° C.

They are much more effective instruments than the water pyrometer described in § 69*a*.

EXAMPLES. XIII.

1. State clearly how you suppose winds to be produced.
2. Wherein does the manner in which heat is usually diffused through liquids and gases differ from the mode of its diffusion through solids?
3. Explain the formation of dew, hoar-frost, and black frost.
4. How do you account for the fact that a cloud is sometimes formed by the mixture of two quantities of air at different temperatures, although neither quantity is quite saturated before the mixture?
5. A building is heated by hot-water pipes. How does the heat get from the furnace of the boiler to a person in the building? What would be the effects on the temperature of the more distant parts of the building of coating the pipes near the boiler (*a*) with woollen felt, (*b*) with dull black lead. (London Matric.)

6. Explain the construction of Siemens's electrical pyrometer. How would you proceed to graduate such an instrument?

7. Explain Professor J. Thomson's theory of atmospheric circulation. Account carefully for the prevailing winds in our latitude.

8. Give an explanation of the Gulf Stream. How does it affect the climate of Western Europe?

9. If 1 lb. of coal in burning will raise 14,000 lbs. of water one degree Fahrenheit, and if an engine can convert one-fifth of the heat given it to useful work, find how much coal must be burnt in raising 1 ton of coal up a pit-shaft 600 yards deep. (London Inter. Sc.)

10. Explain the cause of land and sea breezes.

11. The specific heat of zinc is 0.098, and 280 grams of zinc are raised to the temperature of 97° C., and immersed in 180 grams of water at 14° C., contained in a copper calorimeter weighing 96 grams, the specific heat of copper being 0.095: what will be the temperature of the mixture, supposing that there is no exchange of heat except among the substances mentioned? What is the water equivalent of the calorimeter employed? (London Inter. Sc.)

SCIENCE AND ART PAPERS.

Second Stage, or Advanced Examination.

MAY, 1892.

1. What is meant by the hygrometric state of the air? and state how you would determine it by a condensation hygrometer.

2. Describe a method of measuring the specific heat of a gas at constant pressure.

3. A piece of iron weighing 16 grams is dropped at a temperature of 112.5° C. into a cavity in a block of ice, of which it melts 2.5 grams: if the latent heat of ice is 80, find the specific heat of iron.

4. Two liquids, A and B, are introduced into two barometer tubes, the temperature of each being the same. It is noticed (1) that in both cases a little of the liquid does not evaporate; (2) that the mercury in the tube containing A is more depressed than that in the tube into which B was introduced. Which liquid would you expect to have the higher boiling point? Give reasons for your answer.

5. If the coefficients of cubical expansion of glass and mercury are 0.000025 and 0.00018 respectively, what fraction of the whole volume of

a glass vessel should be filled with mercury in order that the volume of the empty part should remain constant when the glass and mercury are heated to the same temperature?

6. Describe the phenomena observed during the fusion or solidification of an alloy of two metals, and give some explanation of the phenomena.

7. Describe the apparatus used in the liquefaction of oxygen.

8. What do you understand by the first law of thermo-dynamics? and how has its truth been established?

9. Distinguish between a gas and a vapour. How would you show that the pressure of a mixture of gases and vapours between which there is no chemical action, is equal to the sum of the pressures which each would severally exert if alone present?

MAY, 1893.

1. Define the terms "energy" and "work," and explain how, first, the kinetic, secondly, the potential energy of a falling body is measured.

2. Describe the constant volume air-thermometer. How would you use it to find the absolute zero of the air-thermometer?

3. Twenty-five grams of water at 15° C. are put into the tube of a Bunsen ice calorimeter, and it is observed that the mercury moves through 29 centimetres. Fifteen grams of a metal at 100° C. are then placed in the water, and the mercury moves through 12 centimetres. Find the specific heat of the metal.

4. Define the dew-point, and explain how to find the mass of aqueous vapour present in a given volume of air.

5. Define the critical point of a fluid. Give sketches of and point out the differences between the forms of the isothermals of carbonic acid above and below its critical point.

6. Enunciate the axiom on which the second law of thermo-dynamics rests, and show how to deduce from it a proof of the fact that the efficiency of a simple reversible cycle is a maximum.

7. Describe and explain the spheroidal state of a liquid.

8. The latent heat of steam at 100° C. is 536. If a kilogram of water, when converted into saturated steam at atmospheric pressure, occupies 1.651 cubic metre, calculate the amount of heat spent in internal work during the conversion of water at 100° C. into steam at the same temperature.

9. Describe some form of electrical pyrometer.

ANSWERS TO EXAMPLES

- I. (4) $F.^{\circ}$, 212, 32, $-459^{\circ}4$, $-36^{\circ}4$, 392; $R.^{\circ}$, 80, 0, $-218^{\circ}4$, $-30^{\circ}4$, 160. (5) 100, 0, $-35^{\circ}5$, $-273^{\circ}3$. (7) $6\cdot\dot{6}$. (8) 49.
- II. (1) 10'0085 feet, 10'017 feet, 10'019 feet. (2) Density at 212° : density at $32^{\circ} :: 10,000 : 10,024$. (3) 526'02 cubic cm. (4) 0'42 inch, say $\frac{1}{2}$ inch. (5) At 25° C. brass : iron :: 1,000,000 : 1,000,035; at -10° C. brass : iron :: 1,000,000 : 999,912. (6) 0'000000175; with correction (see Errata), 0'0000175. (7) 0'000043, 0'000014.
- III. (2) 1'54 cubic cm. (6) 0'00018.
- IV. (1) 1'464 cubic feet. (3) 718'98 grams. (5) 0'000066. (6) 4'786 grams. (7) 1307'6 inches of mercury = 89 atmospheres nearly. (8) 6432'8 mm. of mercury = 8'5 atmospheres nearly. (11) 0'001294 grams.
- V. (1) 1'72 lb. nearly. (2) $551^{\circ}3$ C. (3) 0'091. (4) 0'639. (5) 0'0000188. (6) 320° C. (7) 0'0329. (8) 0'932. (10) 0'0819. (11) 87'7. (12) 30700 (air), 30545 (hydrogen).
- VI. (2) 158'5. (3) (a) 8° ; (b) $46^{\circ}8$; (c) $7^{\circ}7$; (d) $24^{\circ}7$ (s. h. of phosphorus = 0'147). (4) (a) 277'56 t. u. = 385808'4 foot-pounds; (b) 263'54 t. u. = 366320'6 foot-pounds. (5) 0'110. (6) 5'66 lbs. (10) 740'34 (see § 107). (11) $0^{\circ}95$ C.
- VII. (3) 966'6. (4) $44^{\circ}4$ C. (5) 195 : 112. (7) (a) $21^{\circ}1$ C.; (b) $25^{\circ}6$ C. (8) 624'8, 637. (9) 4'8 lbs. (10) 536'2. (11) 269'4 cubic cm. (13) 228° F., 250° F., 297° F.
- VIII. (12) (1) 16'39; (2) 16'06. (13) 4'27 (air = 1).
- IX. (2) 0'63. (3) 0'75. (4) 6'08 grams. (6) 0'74. (7) 0'102 gram, 79 cubic cm. (8) 100 : 80.
- X. (3) 30'1 thermal units. (4) 16848. (6) 0'153.
- XI. (4) 4 : 1. (15) 0'001417.
- XII. (10) $\frac{110}{424}$. (13) $\frac{160}{534}$, 100,361 foot-pounds. (14) $16^{\circ}9$ C.
- XIII. (9) 1'87 lb. (11) $24^{\circ}5$ C.; 9'12 grams.

Science and Art—

1892. (3) 0'i. (5) $\frac{10}{72}$.

1893. (3) $\frac{3}{29}$. (8) Internal work : external work :: 12'33 : 1, \therefore the amount of heat spent in internal work is $\frac{1233}{1333}$ of the whole = 495,790 t. u.

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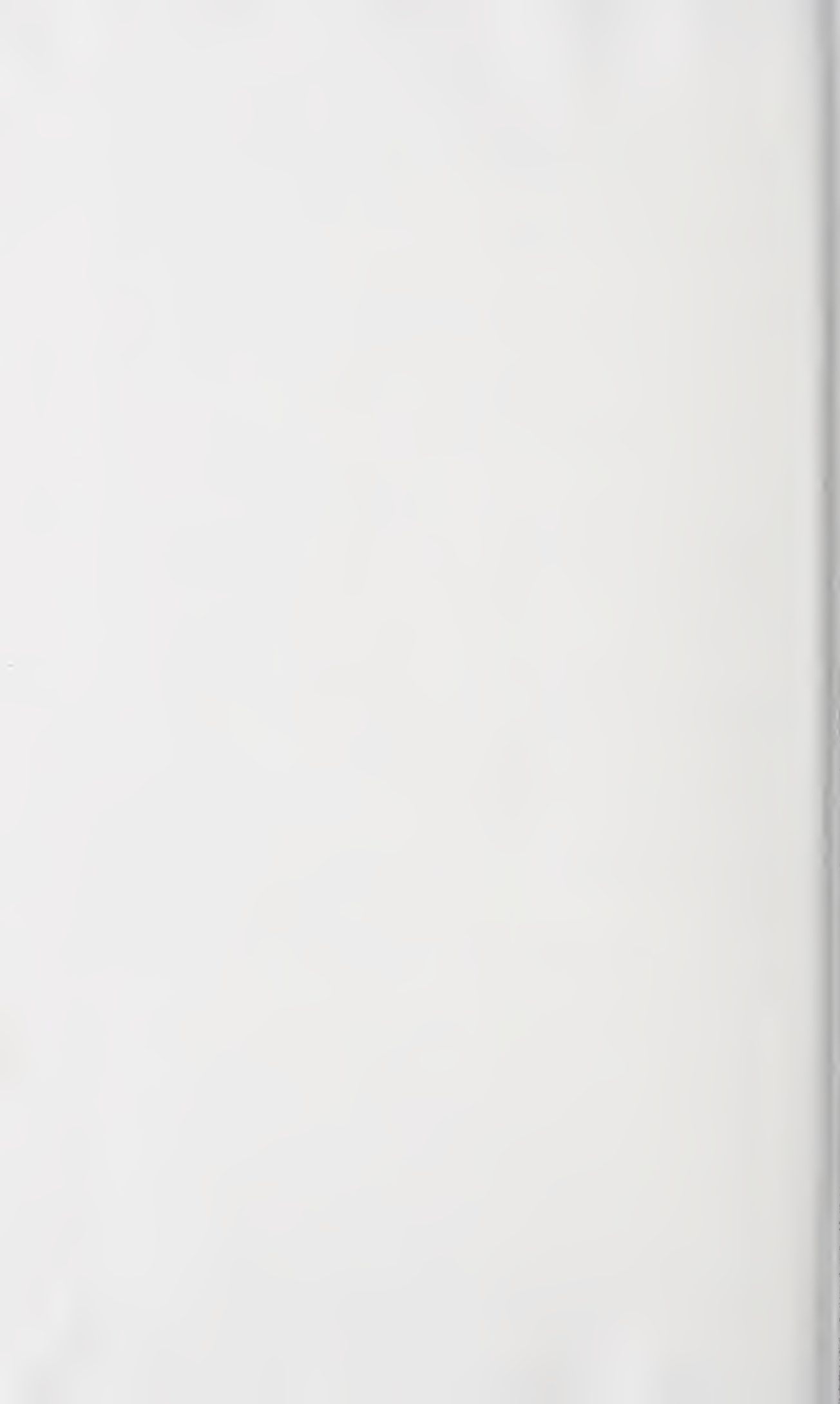
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